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ANNUAL REPORTS
ON THE
PROGRESS OF CHEMISTRY.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1919.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>A.</i>	Abstracts in Journal of the Chemical Society.
<i>Acad. Sci. Fennicae</i>	Acta Societatis Scientiarum Fennicae.
<i>Agric. J. India</i>	Agricultural Journal of India.
<i>Agric. Res. Inst. Pusa</i>	Agricultural Research Institute, Pusa.
<i>Amer. Chem. J.</i>	American Chemical Journal.
<i>Amer. J. Bot.</i>	American Journal of Botany.
<i>Amer. J. Pharm.</i>	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i>	American Journal of Physiology.
<i>Amer. J. Sci.</i>	American Journal of Science.
<i>Anal. Fis. Quim.</i>	Anales de la Sociedad Española Física y Química.
<i>Analyst</i>	The Analyst.
<i>Annalen</i>	Justus Liebig's Annalen der Chemie.
<i>Ann. Bot.</i>	Annals of Botany.
<i>Ann. Chim.</i>	Annales de Chimie.
<i>Ann. Chim. anal.</i>	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Inst. Pasteur</i>	Annales de l'Institut Pasteur.
<i>Ann. Physik</i>	Annalen der Physik.
<i>Ann. Physique</i>	Annales de Physique.
<i>Ann. Report</i>	Annual Reports of the Chemical Society.
<i>Annali Chim. Appl.</i>	Annali di Chimica Applicata.
<i>Apoth. Zeit.</i>	Apotheker-Zeitung.
<i>Arch. Néerland. Physiol.</i>	Archives Néerlandaises de Physiologie de l'homme et des animaux.
<i>Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Arch. Sci. phys. nat.</i>	Archives des Sciences physiques et naturelles.
<i>Arkiv. Kem. Min. Geol.</i>	Arkiv för Kemi, Mineralogi och Geologi.
<i>Atti R. Accad. Lincei</i>	Atti della Reale Accademia dei Lincei.
<i>Ber.</i>	Berichte der Deutschen Chemischen Gesellschaft.
<i>Ber. Deut. bot. Ges.</i>	Berichte der Deutschen botanischen Gesellschaft.
<i>Ber. Deut. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesell- schaft.
<i>Biochem. J.</i>	The Biochemical Journal.
<i>Biochem. Zeitsch.</i>	Biochemische Zeitschrift.
<i>Biol. Zentr.</i>	Biologisches Zentralblatt.
<i>Boll. chim. farm.</i>	Bollettino chimico farmaceutico.
<i>Brit. Pat.</i>	British Patent.
<i>Bull. Assoc. Chim. Sucri.</i>	Bulletin de l'Association des Chimistes de Sucrierie et de Distillerie.
<i>Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>Bull. Soc. chim. Belg.</i>	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. franç. Min.</i>	Bulletin de la Société française de Minéralogie.
<i>Chem. News</i>	Chemical News.
<i>Chem. Weekblad</i>	Chemisch Weekblad.
<i>Chem. Zeit.</i>	Chemiker Zeitung.
<i>Chem. Zentr.</i>	Chemisches Zentralblatt.

* The year is not inserted in references to 1919.

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ABBREVIATED TITLE.	JOURNAL.
<i>Compt. rend.</i>	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Compt. rend. Soc. biol.</i>	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
<i>D.R.-P.</i>	Deutsches Reichs-Patent.
<i>Gazzetta</i>	Gazzetta chimica italiana.
<i>Geol. Mag.</i>	Geological Magazine.
<i>Helv. Chim. Acta</i>	Helvetica Chimica Acta.
<i>J. Agric. Res.</i>	Journal of Agricultural Research.
<i>J. Agric. Sci.</i>	Journal of Agricultural Science.
<i>J. Amer. Chem. Soc.</i>	Journal of the American Chemical Society.
<i>J. Biol. Chem.</i>	Journal of Biological Chemistry.
<i>J. Bd. Agric.</i>	Journal of the Board of Agriculture.
<i>J. Franklin Inst.</i>	Journal of the Franklin Institute.
<i>J. Ind. Eng. Chem.</i>	Journal of Industrial and Engineering Chemistry.
<i>J. Landw.</i>	Journal für Landwirtschaft.
<i>J. Pharm. Chim.</i>	Journal de Pharmacie et de Chimie.
<i>J. Pharm. Expt. Ther.</i>	Journal of Pharmacology and Experimental Therapeutics.
<i>J. Physical Chem.</i>	Journal of Physical Chemistry.
<i>J. Physiol.</i>	Journal of Physiology.
<i>J. pr. Chem.</i>	Journal für praktische Chemie.
<i>J. Soc. Chem. Ind.</i>	Journal of the Society of Chemical Industry.
<i>J. Tokyo Chem. Soc.</i>	Journal of the Tokyo Chemical Society.
<i>J. Washington Acad. Sci.</i>	Journal of the Washington Academy of Sciences.
<i>Koll. Chem. Beihefte</i>	Kolloidchemische Beihefte.
<i>Kolloid Zeitsch.</i>	Kolloid-Zeitschrift.
<i>Kongl., Landtbruks-Akad.</i>	Kongl. Landtbruks-Akademiens Handlingar och Tidskrift.
<i>Landw. Jahrb.</i>	Landwirtschaftliche Jahrbücher.
<i>Landw. Versuchs-Stat.</i>	Die landwirtschaftlichen Versuchs-Stationen.
<i>Lunds. Univ. Årsskr.</i>	Lunds Universitets Års-skrift.
<i>Mem. Coll. Sci. Kyōtō</i>	Memoirs of the College of Science, Kyōtō Imperial University.
<i>Met. and Chem. Eng.</i>	Metallurgical and Chemical Engineering.
<i>Min. Mag.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i>	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Münch. Med. Woch.</i>	Münchener Medizinischer Wochenschrift.
<i>Nachr. Ges. Wiss. Göttingen.</i>	Nachrichten von der Königlichen Gesellschaft der Wissenschaften zu Göttingen.
<i>Ned. Tijdschr. v. Geneesk.</i>	Nederlandsch Tijdschrift voor Geneeskunde.
<i>Nuovo Cim.</i>	Il Nuovo Cimento.
<i>Pflüger's Archiv</i>	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. J.</i>	Pharmaceutical Journal.
<i>Pharm. Weekblad</i>	Pharmaceutisch Weekblad.
<i>Pharm. Zentr.-h.</i>	Pharmazeutische Zentralhalle.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society of London.
<i>Physical Rev.</i>	Physical Review.
<i>Physikal. Zeitsch.</i>	Physikalische Zeitschrift
<i>Proc. Amer. Physiol. Soc.</i>	Proceedings of the American Physiological Society.
<i>Proc. Camb. Phil. Soc.</i>	Proceedings of the Cambridge Philosophical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam.</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Nat. Acad. Sci.</i>	Proceedings of the National Academy of Sciences.
<i>Proc. Roy. Irish Acad.</i>	Proceedings of the Royal Irish Academy.

TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES. ix

ABBREVIATED TITLE.	JOURNAL.
<i>Proc. Roy. Soc.</i>	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i>	Proceedings of the Royal Society of Edinburgh.
<i>Proc. Soc. Exp. Biol. Med.</i>	Proceedings of the Society for Experimental Biology and Medicine.
<i>Sitzungsber. Heidelberger Akad. Wiss.</i>	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
<i>Sitzungsber. K. Akad. Wiss. Berlin</i>	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
<i>Soil Sci.</i>	Soil Science.
<i>Staz. sper. agr. ital.</i>	Stazioni sperimentali agrarie italiane.
<i>Svensk. Kem. Tidskr.</i>	Svenska Kemisk Tidskrift.
<i>T.</i>	Transactions of the Chemical Society.
<i>Trans. Faraday Soc.</i>	Transactions of the Faraday Society.
<i>Trans. Roy. Soc. Canada</i>	Transactions of the Royal Society of Canada.
<i>Zeitsch. anal. Chem.</i>	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i>	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i>	Zeitschrift für anorganische und allgemeine Chemie.
<i>Zeitsch. Elektrochem.</i>	Zeitschrift für Elektrochemie.
<i>Zeitsch. ges. Schiess. u. Sprengstoffw.</i>	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen.
<i>Zeitsch. Kryst. Min.</i>	Zeitschrift für Krystallographie und Mineralogie.
<i>Zeitsch. Nahr.-Genussm.</i>	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. physikal. Chem.</i>	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physikal. Chem. Unterr.</i>	Zeitschrift für den physikalischen und Chemischen Unterricht.
<i>Zeitsch. physiol. Chem.</i>	Hoppe-Seyler's Zeitschrift für physiologische Chemie.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

THE period covered by this Report synchronises with the return of many scientific workers from occupations connected more or less directly with the conduct of war, to conditions of life which may be expected to provide the opportunity for a resumption of scientific investigation for its own sake. In due course, the changed conditions will, presumably, be reflected in the publication of the records of scientific work, but that time has not yet arrived. Apart from a small number of important advances, amongst which may be specially mentioned the researches of Rutherford, which have apparently shown that atoms can be disintegrated by artificial means, the period under review may be justly described as a lean year. Accounts of experimental work dating back to pre-war times are not infrequent and may be expected to continue. On the theoretical side there has been a good deal of speculation and the general trend of this conveys the impression that physical chemistry during the next decade is likely to be very largely influenced by the intrusion of those ideas which are, more or less intimately, associated with the quantum hypothesis. As in previous Reports, no attempt has been made to cover the whole of the ground which might legitimately be said to fall within the limits of this particular section.

Atomic Structure.

The question of atomic structure has been dealt with from different points of view in three lectures which were delivered before the Society during the year by F. Soddy,¹ J. C. Nicholson,² and J. H.

¹ *T.*, 1919, 115, 1.

² *Ibid.*, 855.

Jeans.³ These addresses afford some indication of the contributions which have been made to the solution of the problem of atomic structure by the physical chemist on the one hand, and by the mathematical physicist on the other, and are particularly opportune in the present condition of sub-atomic physics. They serve to indicate the wide divergence of the methods of enquiry by which useful information, positive and negative in kind, has been obtained in reference to the architecture and the physics of the atom.

In Nicholson's address, the problem is discussed from the point of view of emission spectra. The fact that the emission spectra of the structurally simplest elements consist of an infinite number of lines is incompatible with the very small number of possible vibrating parts which are afforded by the atomic models that have been so much in favour during recent years. To get over the difficulty by assuming that the nucleus of the atom is a highly complex structure with an infinite number of degrees of freedom, is to shelve the problem, in that the physics of the nucleus is not yet within the range of our experimental methods. Furthermore, facts are known, amongst which may be cited the Zeeman effect, the Stark effect, and the variations exhibited by the spectra of mixtures of gases, which lead to the conclusion that the electrons are vitally concerned in the emission phenomena. The assumption of an infinite number of states, each of which corresponds with the emission of a finite number of lines, avoids the difficulties otherwise inherent in structures of the simplicity of the Rutherford model atom, and the theories of Ritz and Bohr, which are based on this assumption, have, indeed, achieved a very considerable measure of success. Ritz's theory, which assumes that the vibrations of the electrons are controlled by magnetic forces, is found to be in contradiction with the results of observations on the scattering of α - and β -rays in their passage through the atom, whilst in the more recent theory of Bohr, the simple Rutherford model is retained only by supposing that the motion of the electrons within the atom is governed by laws which differ fundamentally from those of classical mechanics and find their expression in the quantum theory.

Bohr's theory of the origin of spectral lines is criticised by Sir J. J. Thomson⁴ on the ground that dynamical considerations do not provide a basis for the assumption that the only orbits possible to the electrons are those for which the angular momenta are integral multiples of a definite unit, and it is argued that the assumed relation can only be attributed to the action of forces, the existence of which has not been demonstrated. By assuming laws of attraction between positive and negative charges, which become identical

³ *T.*, 1919, 115, 865.

⁴ *Phil. Mag.*, 1919, [vi], 37, 419.

with the law of inverse squares for relatively large distances of separation, but deviate therefrom when the charges are contained within a system of atomic dimensions, Thomson shows that the field of force within the atom may alternate between attraction and repulsion and that the simplest atomic model may give rise to an infinite series of spectral lines. Atomic models characterised by alternate shells of attractive and repulsive forces with intervening positions in which the electrons are in equilibrium, are discussed in considerable detail and are said to afford not only a satisfactory explanation of the complexity and peculiarities of spectral series and of other properties of the atoms, but also to provide a physical basis for Planck's law.

Some of the difficulties which confront the architect who would design a model atom in terms of which the whole of the physical and chemical properties can be satisfactorily interpreted are indicated by Nicholson. In the first place it seems to be established that the dimensions of the nucleus are comparable with those of the electron, and that experiments on the scattering of α - and β -rays are consistent with the view that the electrical forces within the atom are governed by the law of inverse squares, provided that the distances are appreciably greater than are represented by nuclear or electronic dimensions although very small in comparison with atomic magnitudes. The validity of the usual laws of electrical action appears to preclude the possibility of forces of magnetic origin and also the existence of separate rings of electrons. If, however, the electron rings are purely imaginary, the foundation for the widely accepted interpretation of the origin of the characteristic X-radiation disappears, and any attempt to explain this in terms of the nucleus of the atom is irreconcilable with the dimensions which apparently must be assigned to the latter.

With reference to the simplest atomic model, namely, that of the hydrogen atom, Nicholson points out that the reproduction of the Balmer series of lines is but a small step towards the explanation of the spectral relations of this element. The simplicity of the formula renders it comparatively easy to provide a physical basis for the Balmer and other series of similar type, and no fewer than six theories have reached this stage in the interpretation of the emission properties of the hydrogen atom, but none has given any clue to the origin of the secondary spectrum, which Nicholson regards as the real key to the problem of the structure of the hydrogen atom.

According to the views of Jeans, the problem of atomic structure is already narrowed down by the combination of experimental evidence and abstract reasoning to the acceptance of a structure which is that of the Rutherford model, and a mechanism which is that

assumed in Bohr's theory and is based upon and governed by quantum dynamics. Having due regard to the wonderful results which have been achieved by the application of the quantum theory, it may, however, be seriously doubted whether the problem has yet become so circumscribed as to admit of no other basis of interpretation, and in contemplating Jeans' prediction that the fundamental chemical problems will become the province of the mathematician in the very near future, many physical chemists will be inclined to doubt whether the attainment of this condition is yet within measurable distance.

Atomic Disintegration by Collision with α -Particles.

In the early days of the investigation of the phenomena accompanying radioactive disintegration, it was claimed, on more than one occasion, that certain elements had been transformed into others under the influence of the rays emitted by radium or members of the radium series. More recently, the transformation of hydrogen into helium is said to have been effected by the passage of an electric discharge through the former gas. Up to the present time, however, none of these claims has been substantiated by evidence sufficiently strong to permit of artificial transmutation being regarded as an accomplished fact. On the other hand, it seems probable, on the evidence of experiments described by Sir E. Rutherford, that such transmutation is actually possible and that hydrogen is formed from nitrogen under the influence of swiftly moving α -particles.

Observations of Marsden ⁵ showed that the passage of α -particles through hydrogen gave rise to numerous faint scintillations on a zinc sulphide screen placed far beyond the range of the α -particles. Similar results were obtained in the absence of hydrogen and it was found that for the production of these remote "natural" scintillations, the α -ray tube could be replaced by a nickel plate coated with radium-C. From these observations Marsden drew the conclusion ⁶ that the disintegrating radioactive substance was the source of the long-range charged particles. Further experiments by Rutherford ^{7,8} afford evidence, however, that these particles are not liberated simultaneously with the α -particles by the radioactive substance, but are produced by the collision of α -particles with atoms of certain of the light elements when these are brought within the range of the α -particles. Such collisions not only give rise to

⁵ E. Marsden, *Phil. Mag.*, 1914, [vi], 27, 824; *A.*, 1914, ii, 407.

⁶ E. Marsden and W. C. Laxtsberry, *ibid.*, 1915, [vi], 30, 240.

⁷ *Ibid.*, 1919, [vi], 37, 537; *A.*, ii, 256.

⁸ *Ibid.*, 562; *A.*, ii, 258.

charged hydrogen particles of very long range, but similar charged particles of nitrogen and oxygen are produced when these gases are traversed by a stream of α -particles. The nitrogen and oxygen particles give rise to scintillations which also lie outside the range of the α -particles by the action of which they are produced, and it seems probable that a considerable proportion of the scintillations attributed by Marsden to hydrogen atoms are in reality due to charged atoms of oxygen or nitrogen.

Results obtained in the detailed investigation of the nature of the hydrogen particles and of the phenomena associated with their production under the influence of homogeneous α -particles, show that the particles carry a single positive charge, but that the number of the particles and their distribution according to velocity differ very widely from the values which are calculated on the assumption that the nuclei of the hydrogen atom and of the α -particle can be regarded as point charges repelling each other according to the law of inverse squares. For α -particles of long range, the number of hydrogen particles produced is about thirty times as great as that calculated from the simple theory and the velocity with which they are projected forward is approximately the same for all. On the other hand, when the hydrogen particles are produced by the action of α -particles of short range, there is fairly good agreement between the observed and calculated results so far as the distribution of the velocities is concerned, although the total number is considerably in excess of that indicated by theory.

From the experimental data it may be inferred that only 1 in 100,000 of the α -particles (of 7 cm. range), which pass through one centimetre of hydrogen at normal temperature and pressure, gives rise to a charged hydrogen particle, although, over this distance, each α -particle passes, on an average, through the sphere of action of about 10,000 hydrogen molecules. It follows that only one in a thousand million collisions between the α -particles and hydrogen molecules results in the production of a long-range hydrogen particle. These numbers indicate that the distance between the centres of the nuclei of the α -particle and the hydrogen atom in an effective collision is of the order of 3×10^{-13} cm., and it is consequently to be anticipated that each hydrogen atom in a molecule of hydrogen or of a compound containing hydrogen will act as an independent unit. Hydrogen particles should therefore be liberated from all substances containing hydrogen and this is fully borne out by experiment. Incidentally, it may be noted that Rutherford's measurements of the mass, charge and velocity of the hydrogen particles show that the conservation of momentum and energy holds within the limits of experimental error for the collisions which are

in question and that there is no sensible loss of energy due to radiation.

The experiments⁹ made with other elements of low atomic weight show that if long-range particles are produced in the case of helium, the number must be very small compared with that produced in hydrogen, and when the α -particles were made to pass through thin layers of salts of lithium, glucinum, and boron, negative results were also obtained. Similarly, no evidence of singly-charged carbon atoms was obtained when the α -particles were passed through carbon dioxide, although, as already mentioned, both nitrogen and oxygen give rise to swiftly moving atoms of the respective elements. The number of these produced per unit of path is about the same as that produced in hydrogen.

In seeking for an explanation of the origin of the "natural" scintillations given by radium-*C* at distances far beyond the range of the α -particles, Rutherford found¹⁰ that the number of these scintillations is very considerably increased when the α -particles are made to pass through a layer of air or nitrogen. The increase in the number of these scintillations is greater for nitrogen than for air by about twenty-five per cent., and the origin of the effect is definitely traced to the gas traversed by the particles. The brightness of the scintillations and the range of the particles indicate that these are in all probability charged hydrogen atoms and Rutherford considers that it is difficult to avoid the conclusion that they have been produced by the collision of the α -particles with nitrogen atoms. The determination of the mass and charge of the particles may be necessary to establish the identity quite definitely, but on the evidence already adduced it would seem that there can be little doubt that the hydrogen atoms are produced by the disintegration of nitrogen atoms, and it may be inferred that the hydrogen nucleus is a constituent part of the nitrogen nucleus. In this connexion it may be noted that the majority of the light atoms have atomic weights represented by $4n$ or $4n+3$, where n is a whole number, and that nitrogen is the only atom represented by $4n+2$. The formula is consonant with the helium-hydrogen hypothesis according to which the nitrogen nucleus may be supposed to consist of three helium and two hydrogen nuclei, and if it is assumed that the hydrogen nuclei lie outside the main system of mass 12, the disruptive effect of the swiftly moving α -particles is readily intelligible.

⁹ *Phil. Mag.*, 1919, [vi], **37**, 571; *A.*, ii, 259.

¹⁰ *Ibid.*, 581; *A.*, **8**, 260.

X-Ray Spectra.

The accuracy with which measurements of wave-length in high frequency spectra can be effected appears to have been very considerably increased by a method described by M. Siegbahn,¹¹ in which the angle of reflection, instead of being determined geometrically as in the older methods, is derived from observations of the angle through which the photographic plate must be turned so that impressions of the n th order reflection are received on both sides of the direct ray. By turning the plate through 4ϕ , where ϕ is the angle of reflection, and the crystal through $2\phi + 180^\circ$, the lines on both sides of the direct ray should coincide. In practice, the plate is turned through an angle approximately equal to 4ϕ and from the distance between the lines, the difference between the approximate and the true angle of reflection can be estimated.

The accurate wave-length data obtained for lines of the K -group by the use of Siegbahn's X -ray spectrograph have been used in a comparison of the formulæ proposed for the series lines by Moseley, Sommerfeld, Debye and Kroo, respectively. The comparison is decidedly favourable to J. Kroo's formula,¹² in that the differences between the calculated and observed values for elements of atomic number 17 to 29 are less than 0.2 per cent. when this formula is used. The fine structure of the lines in the K -group has also been examined with the result that the difference between the wave-lengths of the α_1 - and α_2 -lines in the X -ray spectrum of copper is found to agree remarkably closely with the value previously calculated by Sommerfeld.

Spectral Emission in an Electrical Field.

In continuation of previous experiments, Stark¹³ has investigated the influence of an electric field on lines of the Fowler helium series. The effect of the field is very similar to that previously found in experiments on the lines of the Balmer hydrogen series, the resolution in both cases being symmetrical.

The Stark effect has been examined in considerable detail by Japanese experimenters. The data for hydrogen,¹⁴ helium,¹⁵ oxygen

¹¹ *Phil. Mag.*, 1919, [vi], 37, 601; *A.*, ii, 261.

¹² *Physikal. Zeitsch.*, 1918, 19, 307; *A.*, 1918, ii, 303.

¹³ J. Stark, O. Hardtke, and G. Liebert, *Ann. Physik*, 1918, [iv], 56, 569; *A.*, ii, 37.

¹⁴ T. Takamine and N. Kokubu, *Mem. Coll. Sci. Kyoto*, 1919, 3, 271; *A.*, ii, 379.

¹⁵ *Ibid.*, 1919, 3, 275; *A.*, ii, 379.

and nitrogen,¹⁶ argon,¹⁷ lithium,¹⁸ calcium and magnesium¹⁹ afford evidence that the phenomenon is of complex character, and as yet it does not appear to be possible to deduce general conclusions.

From observations²⁰ on the series lines of zinc, mercury, lithium and calcium, it appears that the effect of an electric field is to cause the pressure displacement and the unsymmetrical broadening to increase along a series with increasing member number and decreasing wave-length. The fact that the electrical displacement, the displacement produced by an increase of pressure, and the dissymmetry are all of the same sign, is regarded as evidence in favour of Stark's hypothesis that the pressure displacement and the unsymmetrical broadening are due to an intramolecular electric field.

On the assumption that broadening of spectral lines is to be attributed to an intra-molecular electric field, P. Debye²¹ has made some interesting calculations relative to the magnitude of this field in the case of charged and uncharged molecules. Taking the molecular radius as 10^{-8} cm. it is calculated that the intra-molecular field strength is of the order of 1,350,000 volts per centimetre in the case of ions, 40,500 volts in the case of uncharged molecules with an electric moment, and 1,200 volts in the case of molecules which have no electric moment. The electric moments of the molecules of ammonia and sulphur dioxide are of the anticipated order of magnitude, and experiments show the existence of an intra-molecular field, the intensity of which corresponds with about 40,000 volts per centimetre.

Valency and Duplex Affinity.

The old conception of duplex affinity has been modified in many and various ways since it was originally put forward by Berzelius. In the particular form²² which has been given to the theory by S. H. C. Briggs, due regard is paid to modern views on the structure of the atoms and the utility of the modified conception has already been demonstrated.

In a further contribution²³ to the theory, the secondary affinity of positively charged atoms is more particularly considered. Assum-

¹⁶ U. Yoshida, *Mem. Coll. Sci. Kyoto*, 1919, **3**, 287; *A.*, ii, 379.

¹⁷ T. Takamine and N. Kokubu, *ibid.*, 281; *A.*, ii, 378.

¹⁸ U. Yoshida, *ibid.*, 1918, **3**, 161; *A.*, ii, 380.

¹⁹ T. Takamine and N. Kokubu, *ibid.*, 173; *A.*, ii, 380.

²⁰ M. Ritter, *Ann. Physik*, 1919, [iv], **59**, 170; *A.*, ii, 380.

²¹ *Physikal. Zeitsch.*, 1919, **20**, 160; *A.*, ii, 211.

²² *T.*, 1919, **115**, 253. Compare *Ann. Report*, 1917, 10.

²³ *Ibid.*, 278.

ing that the atoms can be regarded as spheres, the radii of which are large enough to include all the structural elements (valence electrons, etc.), and that the nucleus is situated at the centre and that the dimensions of the nucleus are extremely small compared with the volume of the atom as a whole, it follows that, in a positively charged atom, the charge may be considered to be distributed uniformly over the surface of the atom in so far as the influence on other atoms is concerned. In this respect the secondary negative affinity differs essentially from the secondary positive affinity, which cannot be supposed to be uniformly distributed over the atomic surface and the difference appears to be of considerable importance in the building up of inorganic compounds.

Simple geometrical considerations based on the above view of the mode of action of secondary affinity are shown to lead to a simple interpretation of the relationship between the atomic volumes of the elements and the electrolytic properties of their compounds; of the non-polar character and volatility of specially symmetrical compounds such as methane, carbon tetrachloride, sulphur hexafluoride, tungsten hexafluoride, ruthenium tetroxide, and osmium tetroxide; of Werner's co-ordination numbers and the co-ordination formula; and of the increasing acidity of the hydroxides of an element with increasing number of the oxygen atoms.

The application of Briggs's views to the hydrogen atom is of particular interest. Since the hydrogen ion consists of a positive nucleus only, the positive charge must be considered as concentrated in the nucleus instead of being distributed over the surface of a comparatively very large sphere. Such a nucleus will attract to itself lines of force binding the atoms of a molecule brought into its vicinity, and in this way, it is possible to explain the catalytic activity of acids. It is shown that the theory is in general agreement with the results which have led to the recognition of the catalysing power of acids both in the ionised and non-ionised form, and with the variation in the activity of a given acid with change of solvent.

In an attempt to account for the valencies of the metals in the complex metal ammine-compounds, R. De²⁴ considers that a distinction should be drawn between free and bound valence electrons.

In the case of chloropentammine-cobaltic chloride, $\left(\text{Co}^{\text{5NH}_3}_{\text{Cl}}\right)\text{Cl}_2$, the cobalt atom is supposed to contain three valence electrons, one of which is bound to the chlorine atom in the complex, whilst the other two, situated outside the complex, are free and correspond with valencies of the polar type. The ammonia molecules are con-

²⁴. *T.*, 1919, 115. 127.

sidered to be bound to the cobalt by valencies of the non-polar type.

Measurements²⁵ of the solubility of organic acids and phenols in aqueous solutions containing varying amounts of hydrochloric, nitric, sulphuric, acetic, formic or lactic acid afford evidence that in such solutions compounds are formed between the solute and the solvent acid. The solubility curves can be readily interpreted in terms of this view when due consideration is given to the common ion influence and the relative solvent capacities of water and the acid with which it is associated. In accordance with earlier views relative to the interpretation of such solubility effects, it is suggested that the organic acids and phenols contain a basic oxygen atom, in virtue of which these substances form salts of the oxonium type with the solvent acid, the oxygen becoming quadrivalent.

Rotatory Dispersion Power.

The fact that the rotatory dispersion of organic compounds of simple structure can be satisfactorily represented by Drude's formula $\alpha = k/(\lambda^2 - \lambda_0^2)$, in which k (the rotation constant) and λ_0 (the dispersion constant) are constants peculiar to the substance examined, was demonstrated some years ago²⁶ by reference to the data for substances containing one or more asymmetric carbon atoms associated with the simplest radicles such as H, OH, and the like. The publication by H. Rupe²⁷ of measurements, for four different wave-lengths, of the optical rotatory powers of compounds belonging to the terpene series, which included derivatives of methylenecamphor, menthol and its esters, myrtenol and its esters, hydrocarbons derived from citronellaldehyde, camphor, pulegone and carvone, has provided Lowry²⁸ with an opportunity of testing the validity of the Drude formula for compounds in which the above elements of structural simplicity are no longer present.

The experimental data in question have been previously analysed by A. Hagenbach,²⁹ who showed that the dispersion ratio for any given pair of wave-lengths has the same value in each series of closely related compounds. It follows from this that the rotatory dispersion of any member of such a series can be expressed by the equation $\alpha = c\phi(\lambda)$ in which c is a constant characteristic of the particular compound. Hagenbach failed to discover the nature of

²⁵ J. Knox and Miss M. B. Richards, *T.*, 1919, **115**, 508.

²⁶ T. M. Lowry, *ibid.*, 1913, **103**, 1067.

²⁷ *Annalen*, 1915, **409**, 327; *A.*, 1915, ii, 717.

²⁸ T. M. Lowry and H. H. Abram, *T.*, 1919, **115**, 300.

²⁹ *Zeitsch. physikal. Chem.*, 1915, **89**, 570; *A.*, 1915, ii, 302. *Annalen*, 1915, **409**, 349, 351.

the function ϕ , but Lowry's calculations show unmistakably that the connexion between α and λ is given by a one-term equation of the Drude type. The closeness of the agreement in the case of 33 of the 36 compounds examined is such that the "simple" character of the rotatory dispersion could only be called in question, if the exactness of the data, or the spectral region covered by the measurements, were considerably increased. For the three remaining compounds, the rotatory dispersion is "complex."

In the compounds investigated by Rupe, new radicles are introduced at points considerably removed from the asymmetric carbon atom and the constancy of the dispersion ratio is doubtless connected with this circumstance, for in the secondary alcohols, previously investigated, the asymmetric carbon atom is directly associated with a "growing chain" and the dispersion ratio varies from member to member of the series until the chain in question has established itself as the heaviest radicle attached to the asymmetric carbon atom. The lowest homologues in such a series have thus an abnormally high rotatory dispersion, but there is no question of any change in the character as defined by the Drude equation.

In a paper describing the results of an investigation of the rotatory dispersion of butyl, heptyl, and octyl tartrates, P. F. Frankland and F. H. Garner³⁰ point out that the simple Drude formula does not afford a satisfactory basis for the classification of optically active substances, in that the character of the dispersion exhibited by a particular substance varies with the temperature. Butyl tartrate, for example, exhibits "simple" rotation dispersion at high temperatures, but at low temperatures the dispersion is "complex." Whilst admitting the utility of the distinction between "simple" and "complex" dispersion, the authors consider that there is much to be said in favour of the retention of the older terms "normal" and "anomalous." On their view a compound should be described as "anomalous" if its rotatory dispersion curve shows a maximum and as "normal" if no maximum is present. An "anomalous" compound is thus always "complex"; whilst a "normal" compound is "simple" or "complex" according to its behaviour when subjected to the test of the Drude formula.

Optical Rotatory Power.

Observations³¹ on the rotatory power of derivatives of phenyliminocamphor are found to afford little support for Frankland's views³² relative to the influence of substitution in the ortho-, meta-

³⁰ *T.*, 1919, 115, 636.

³¹ B. K. Singh and J. K. Mazumder, *ibid.*, 566.

³² Compare *T.*, 1912, 101, 654.

and para-positions. Apart from the irregularities which are disclosed when corresponding *o*-, *m*-, and *p*-derivatives are compared with the parent substance, it is found that there is no simple connexion between the nature of the substituting element or group and its influence on the rotatory power. In the case of ortho-compounds, arranged in the order of increasing rotatory power, the sequence of the substituent elements or groups is $\text{Cl} < \text{OCH}_3 < \text{CH}_3 < \text{Br} < \text{H}$, whilst for meta-compounds the order is $\text{Cl} = \text{Br} < \text{CH}_3 < \text{H}$, and for para-compounds $\text{Br} < \text{H} < \text{Cl} < \text{CH}_3 < \text{OCH}_3$. The supposition³³ that ortho-substitution has greater influence than substitution in the meta- or para-position is also not supported by the authors' data.

Osmotic Properties of Disperse Systems.

According to Wo. Ostwald and K. Mundler³⁴ the observed osmotic pressures of disperse systems can be represented quite generally by an equation of the form $P = RTc_1 + kc_2^n$, in which the first term corresponds with the true osmotic pressure of the disperse phase, whilst the second term represents the solvation or swelling pressure. The osmotic concentration is denoted by c_1 , the swelling concentration by c_2 , whilst k and n are constants. For molecular or suspensoid dispersoids of small concentration, the second term is relatively of little account, and the osmotic equation assumes the form of the simple gas equation. On the other hand, when concentrated dispersoids, or, more particularly, swelling gels are in question, the osmotic concentration is small, and the osmotic equation becomes $P = kc_2^n$. This equation has been shown³⁵ previously to represent satisfactorily the connexion between swelling pressure and concentration when applied to observations on the swelling of gelatin and caoutchouc.

When the above osmotic equation is applied to the osmotic pressures recorded by Morse and by Lord Berkeley and Hartley for solutions of sugars and calcium ferrocyanide, it is found that there is a very close agreement between the calculated and observed pressure values. For the most concentrated of the solutions examined, the swelling pressure term has a greater value than that which represents the true osmotic pressure. The value of n varies with the nature of the dispersoid substance and with the temperature, but is usually greater than two and less than three.

It is well known that the simple formula $\Delta = 1000Kw/mW$ ex-

³³ J. B. Cohen, *T.*, 1910, **97**, 1737; 1911, **99**, 1060.

³⁴ *Kolloid Zeitsch.*, 1919, **14**, 7; *C.A.*, ii, 185.

³⁵ E. Posnjak, *Koll. Chem. Beihefte*, 1912, **3**, 417; *A.*, 1912, ii, 912.

pressing the connexion between the lowering of the freezing point and the concentration does not hold for moderately dilute solutions of many substances, even when these are of the non-associating type and do not dissociate. If W , the weight of the solvent in which w grams of the solute of molecular weight m are dissolved, is replaced by $W + bw$, the formula becomes $\Delta = 1000Kw/m(W + bw)$, in which b is a constant, dependent, both in respect of sign and magnitude, on the nature of the solvent and of the dissolved substance. This modified formula is found³⁶ to give very satisfactory results in the reproduction of the actual freezing-point depressions.

When several different substances are simultaneously present in the same solution, the lowering of the freezing point is given by the corresponding formula,

$$\Delta = 1000K(w_1/m_1 + w_2/m_2 + w_3/m_3 \dots) / (W + b_1w_1 + b_2w_2 + b_3w_3 \dots)$$

in which w_1, w_2, w_3, \dots are the weights of the several dissolved substances, m_1, m_2, m_3, \dots their molecular weights, and b_1, b_2, b_3, \dots the values of the constant " b ." Measurements of the freezing points of mixed solutions are found to be in close agreement with the values calculated from this formula.

As an aid to analytical work, freezing-point measurements have found increasing application in recent years. When the components of a mixture show a close approximation in their chemical and physical properties, it will often be found that freezing-point methods can be applied with considerable advantage. It has been shown,³⁷ for instance, that binary and ternary mixtures of the three cresols can be analysed without difficulty by recourse to freezing-point measurements and it may be anticipated that, in a general way, the analysis of mixtures of this type will be facilitated by the use of freezing-point methods. As an illustration of a particular mode of procedure in the application of freezing-point methods, reference may be made to a recently published paper³⁸ containing results obtained by C. E. Fawsitt.

Electrolytes and the Dilution Law.

It is probably not quite generally realised that the requirements of the law of mass action are satisfied by the experimental data for the ionisation of weak acids and bases in aqueous solutions of varying concentration very much more closely than by the corresponding data for the variation of the thermal dissociation in any gaseous system which has yet been subjected to exact measurement. It is

³⁶ C. E. Fawsitt, *T.*, 1919, 115, 700.

³⁷ H. M. Dawson and C. A. Mountford, *ibid.*, 1918, 113, 935.

³⁸ *Ibid.*, 1919, 115, 80f.

probable that this is equally true for non-ionic equilibria in liquid systems. The point has recently been emphasised in a review³⁹ of the literature on the dilution law contributed to a recent discussion on the present position of the theory of ionisation. The closeness of the agreement in the case of weak electrolytes seems to give to the anomalous behaviour of the strong electrolytes an increased significance.

Of the many formulæ which have been put forward to represent the variation of the ionisation of strong electrolytes with the concentration, the only one, apart from the Ostwald formula, which has any theoretical foundation, is that based on the assumption that the ionisation of the molecules of the electrolyte is not merely determined by the intrinsic instability of the molecules, but that, concurrently, ions are produced as the result of collision between molecules and ions. The assumption leads to the formula

$$\alpha^2/(1-\alpha)(v+\epsilon\alpha)=K,$$

in which ϵ is a constant the magnitude of which is determined by the ionising activity of the ions. It cannot be said that this formula has met with any great measure of success, and it has yet to be shown that the behaviour of the strong electrolytes can be satisfactorily explained on the basis of the view that these are completely ionised. The novel features of Ghosh's theory, in which complete ionisation is assumed, were referred to in last year's Report.⁴⁰ Since that time, the theory has been critically examined by Partington, who draws the conclusion that the generalisations which may be deduced from Ghosh's formulæ are in no case in agreement with the experimental data within the limits of error. Furthermore, the theory assumes that the forces acting between the components of binary molecules may be represented as the forces between electrical doublets and that the work of electrical separation is the equivalent of the heat of ionisation, but if a comparison is made between the work which must be done to separate the ions according to Ghosh's formula and the heat of ionisation, which may be readily obtained from available thermal data, the result is entirely unfavourable to the assumption that electrical forces only are operative in solutions of electrolytes, an assumption which appears to be fundamental in the theory put forward by Ghosh.

Adsorption.

In spite of the fact that the thermodynamic relation of Gibbs has been shown to be applicable to the actual surface effect at a liquid-liquid interface, it must be admitted that, on experimental grounds,

³⁹ J. R. Partington, *Trans. Faraday Soc.*, 1919, 15, 98.

⁴⁰ *Ann. Report*, 1918, 11.

the thermodynamic relation is not of immediate practical importance for the very large group of adsorption systems in which the adsorbent is a solid. For solid adsorbents the occurrence of adsorption is indeed generally recognised by the applicability of the purely empirical relation which is commonly referred to as the "exponential" law. It might almost be said that this relation has come to be regarded by some chemists as the basis of a method for recognising and defining adsorption phenomena. A satisfactory theoretical interpretation of the "exponential" formula has, however, yet to be put forward.

Langmuir's speculations⁴¹ relative to the nature of the adsorption layer seem to have awakened a renewed interest in the consideration of the problem on a molecular-kinetic basis, and in some recent publications the phenomena have been examined from this point of view by A. M. Williams.⁴² On the assumption that adsorption is due to the action of cohesive forces which are identified with van der Waals' "*a*," and that there is a thin layer at the surface of the adsorbent in which the molecules of the adsorbed substance oscillate, the author derives equations⁴³ which give the connexion between the adsorption (α) and the concentration (c) of the substance in the surrounding medium at constant temperature, and also the connexion between the concentration and the absolute temperature (T) when the quantity of substance adsorbed by unit quantity of adsorbent is constant.

The equation for the adsorption isotherm is $\log \alpha/c = A_0 - A_1 \alpha$ in which A_0 and A_1 are factors which depend only on the temperature, whilst the equation for the adsorption isostere is $\log \alpha/c = B + A/T$ in which B and A are factors depending only on the degree of adsorption α .

By reference to the data given by various observers for the adsorption of argon, methane, carbon monoxide, carbon dioxide, nitrogen and ammonia by amorphous carbon, it is shown that the experimental numbers are in good agreement with these equations when the temperature is above the critical temperature of the gas concerned.

In a later paper,⁴⁴ from a consideration of the isostere of zero adsorption, it is shown that A should be proportional to \sqrt{a} . The value of A , derived from Miss Homfray's experimental data,⁴⁵ and the corresponding values of " a " are shown in the following table

⁴¹ *J. Amer. Chem. Soc.*, 1916, **38**, 2221; *A.*, 1917, ii, 19.

⁴² *Proc. Roy. Soc. Edin.*, 1919, **39**, 48; *A.*, ii, 392.

⁴³ *Proc. Roy. Soc.*, 1919, [A], **96**, 287; *A.*, ii, 496. ⁴⁴ *Ibid.*, 298; *A.*, ii, 496.

⁴⁵ *Zeitsch. physikal. Chem.*, 1910, **74**, 129; *Proc. Roy. Soc.*, 1910, [A] **84**, 99; *A.*, 1910, ii, 771.

together with the values of A/\sqrt{a} , and it is apparent that the variations of this ratio are inconsiderable, although the values of A and a differ widely.

Adsorbed Gas.	He	A	N ₂	CO	CH ₄	CO ₂	C ₂ H ₄
A	134	822	856	933	1081	1245	1631
a	0.000069	0.00259	0.00268	0.00280	0.00367	0.00701	0.00806
$A/\sqrt{a} \cdot 10^{-4}$	1.61	1.62	1.65	1.76	1.78	1.49	1.73

In one of a series of papers contributed to a discussion, arranged by the Faraday Society, on the subject of occlusion, figures are given⁴⁶ which illustrate the extreme slowness with which equilibrium is attained in certain heterogeneous systems. Observations,⁴⁷ made in 1907, on the removal of iodine from benzene and toluene solutions by amorphous carbon, in the form of an impalpable powder, showed that there is a rapid condensation of iodine on the surface of the solid followed by a slow diffusion. After an interval of eleven years, the solutions have been re-examined and it is found that the diffusion process is still in progress.

Colloids.

The X-ray interference method⁴⁸ employed by Debye and Scherrer in the morphological investigation of finely divided substances has been applied⁴⁹ in an attempt to determine the size and internal structure of typical inorganic and organic colloids. Colloidal silver and gold are found to be definitely crystalline, the interference figures obtained in the examination of these substances corresponding with a space lattice which is identical with that indicated by observations on macroscopic crystals of the metals. The characteristic space lattice is indeed shown by gold particles which are too small to be observed with the ultra-microscope. Typical organic colloids, such as albumin, gelatin, casein, cellulose and starch afford no evidence of internal structural regularity and it is probable that the colloidal particles of these substances consist of individual molecules or of irregularly orientated groups of molecules. Old specimens of silicic acid and stannic acid gels show well marked interference figures in addition to the characteristics of amorphous substances, and the author suggests that the behaviour of these towards X-rays is indicative of incipient crystallisation of the originally amorphous aggregates.

Some observations on the behaviour of various colloids towards the blue solution which is obtained by the action of acids on

⁴⁶ J. W. McBain, *Trans. Faraday Soc.*, 1919, **14**, 202; *A.*, ii, 449.

⁴⁷ O. C. M. Davis, *T.*, 1907, **91**, 1666.

⁴⁸ Compare *Ann. Report*, 1917, 9.

⁴⁹ P. Scherrer, *Nachr. Ges. Wiss. Göttingen*, 1918, 96; *A.*, ii, 274.

Congo-red, are cited⁵⁰ in support of the view that chemical reaction in heterogeneous systems is preceded by the formation of an adsorption compound. It is found that acid gels, when free from electrolytes, do not absorb the dye-acid and do not cause any change in colour or heating, whereas the blue acid is adsorbed by basic gels which assume the red colour characteristic of the Congo-acid salts when the temperature is raised. Other dyes show similar differences in their behaviour towards the acid and basic groups of gels.

In reference to the mechanism of flocculation, it has been stated⁵¹ that the Brownian movements are diminished by the addition of a coagulating electrolyte, but this view is said⁵² to be refuted by microscopic observations which show that coagulation precedes and is therefore in all probability the cause of the diminution in the amplitude of the Brownian movements.

Our knowledge of the physical chemistry of colloidal electrolytes has been extended by a further investigation⁵³ of the electrical conductivities of soap solutions and the determination of their freezing points. To account for the high electrical conductivity, relatively low osmotic activity and feeble alkalinity of soap solutions, it has been suggested that these are characterised by the presence of ionic micelles of high valency, electric mobility and degree of solvation. It is supposed that the ionic micelle results from the aggregation of ordinary ions—in this case the organic acid ions—forming a nucleus on which is condensed a large number of molecules of water and of colloidal soap. The mechanism which results in the production of coherent aggregates from similarly charged particles is not made clear, but the formation of such ionic micellar aggregates is said to be so complete in the case of the higher soaps at the ordinary temperature, that the only other constituent of the solutions is the potassium, sodium, or ammonium ion, as the case may be. The mobility of the micelle is such that the soaps are moderately good conductors even in concentrated solution. As compared with ordinary electrolytes the conductivity exhibits, however, certain anomalies. It is found, for instance, that the conductivity, after passing through a minimum, rises with increase in concentration to a maximum, a phenomenon not otherwise met with in aqueous solutions if we except the behaviour⁵⁴ of hexadecanesulphonic acid, which is also a soap. This increase in conductivity with increase in concentration is said to be due to the replacement

⁵⁰ E. Wedekind and H. Rheinboldt, *Ber.*, 1919, **52**, [B], 1013; *A.*, ii, 270.

⁵¹ Compare H. W. Woudstra, *Chem. Weekblad*, 1918, **15**, 679; *A.*, ii, 52.

⁵² D. J. Hissink, *ibid.*, 1919, **16**, 20; *A.*, ii, 52.

⁵³ J. W. McBain, Miss M. E. Laing and A. F. Titley, *T.*, 1919, **115**, 1279.

⁵⁴ A. Reyckler, *Bull. Soc. chim. Belg.*, 1913, **27**, 113; *A.*, 1913, i, 699.

of simple organic acid ions by ionic micelles of higher mobility, the effect of which is more than sufficient to counterbalance the decreasing ionisation.

It is suggested that the soaps are typical of a very large group of substances and that an extension of the ionic micelle hypothesis may provide a basis for the interpretation of the behaviour of all charged colloids.

Chemical Change and Radiant Energy.

In a comprehensive memoir J. Perrin⁵⁵ has made an attempt to explain the various phenomena associated with the physical and chemical transformations of matter on the assumption that these are determined by the absorption and emission of radiant energy. It is unfortunate that the author has failed to take into account the notable advances which have already been made in the interpretation of physico-chemical phenomena by the application of radiation hypotheses which in essentials do not differ greatly from that which he has himself elaborated. No reference is made to Lewis's work and Einstein is ignored. The quantum hypothesis is referred to, but the author appears to be mainly concerned with certain obscurities incidental to the origin of the idea of quanta in Planck's hypothesis. The failure to recognise the actual position of affairs in the application of the quantum hypothesis is regrettable, but, nevertheless, it must be conceded that Perrin's contribution to the subject is in some respects novel, and affords a coherent interpretation of a large number of phenomena, including chemical change, fluorescence,⁵⁶ phosphorescence, radioactive disintegration, changes in the state of aggregation and so forth. In this Report the exigencies of space will only admit a brief reference to Perrin's views in so far as these relate to radioactive changes. These transformations, like all other chemical changes, are supposed to be due to the absorption of radiation by the disintegrating radioactive element. The active rays, for which the name ultra-X-rays is suggested, are of highly penetrating character, and their frequency is very much greater than that of the rays which are ordinarily responsible for chemical reactions. In this very high frequency of the radiation which is responsible for radioactive disintegration is to be found an explanation of the fact that the velocity of such disintegration processes is independent of the temperature over the range which can be subjected to experiment. In Perrin's view, the radioactive atoms are stable systems and the disintegra-

⁵⁵ *Ann. Physique*, 1919, [ix], 11, 5; *A.*, ii, 177.

⁵⁶ Compare *ibid.*, 1918, [ix], 10, 133; *A.*, 1918, ii, 448.

tion process is not, as usually supposed, a highly exothermic reaction, but a change in which a very considerable amount of energy is absorbed.

The investigation of the combination of hydrogen and chlorine under the influence of light may be said to have entered on its present phase with the recognition of the important part played by small quantities of foreign substances which retard or inhibit the reaction. Oxygen is a substance of this type and it has been shown that in the presence of small quantities of oxygen (0.1 to 1 per cent.), the rate of combination of hydrogen and chlorine is approximately inversely proportional to the oxygen-content of the gas mixture. Chapman and his collaborators have also shown⁵⁷ that if the concentrations of the chlorine and of the oxygen are constant, the rate of the reaction is nearly independent of the concentration of the hydrogen, provided that this is not very small.

Combining these results with the data furnished by experiments of M. Bodenstein and W. Dux,⁵⁸ who claim to have found that the reaction is of the second order when the hydrogen and chlorine are present in equivalent proportions, it follows that the velocity of the photochemical change is proportional to the square of the concentration of the chlorine. Later observations made by Chapman and Whiston⁵⁹ do not, however, confirm the results obtained by the German investigators. On the contrary, it is found that within wide limits of concentration of the interacting gases the rate of formation of hydrogen chloride is given with fairly close approximation by the equation $d[\text{HCl}]/dt = k \cdot I \cdot [\text{Cl}_2]/[\text{O}_2]$, in which k is a constant and I the intensity of the radiation. Since $I \cdot [\text{Cl}_2]$ is a measure of the rate at which the radiant energy is absorbed, it follows that the rate of formation of hydrogen chloride is directly proportional to the radiation absorbed and inversely proportional to the concentration of the oxygen retarder. This result is explicable on the hypothesis that the radiant energy is absorbed by the chlorine molecules and that the active molecules which react with hydrogen represent partly deactivated molecules which have escaped the inhibiting influence of the impurities in the reacting mixture. The hypothesis in question is plausible enough, but its significance is difficult to estimate because of its lack of precision. A possible explanation of the divergent observations of Bodenstein and Dux is to be found in the gradual production of inhibitors during the insolation of the reacting mixture.

The application of the quantum hypothesis to photochemical

⁵⁷ D. L. Chapman and L. K. Underhill, *T.*, 1913, 103, 496.

⁵⁸ *Zeitsch. physikal. Chem.*, 1913, 85, 297; *A.*, 1913, ii, 1039.

⁵⁹ *T.*, 1919, 115, 1264.

reactions leads, as is well known, to the relation known as the law of photochemical equivalence, which may be expressed in the form $Q = Nh\nu$ where Q denotes the energy absorbed per gram-molecule, N the Avogadro number, h Planck's constant, and ν the frequency of the absorbed radiation. From this equation it is possible to calculate the quantity of the photochemically sensitive substance which is transformed by a given amount of absorbed energy. In the case of the reaction between hydrogen and chlorine, the quantity of hydrogen chloride produced is vastly in excess of the value⁶⁰ calculated on this basis, and W. Nernst,⁶¹ on the assumption that the primary reaction consists in the dissociation of the chlorine molecule into atoms, attributes this to a succession of secondary changes represented by the equations $\text{Cl} + \text{H}_2 = \text{HCl} + \text{H}$ and $\text{H} + \text{Cl}_2 = \text{HCl} + \text{Cl}$. It is calculated that the former change is accompanied by the liberation of 25,000 calories and the latter by 19,000 cal., and these large exothermic values of the secondary reactions are supposed to be responsible for the inapplicability of the Einstein relation to the hydrogen chloride which is actually formed. The very limited reaction which occurs when hydrogen and bromine are exposed to light is, on the same view, determined by the endothermicity of the reaction $\text{Br} + \text{H}_2 = \text{HBr} + \text{H}$, for which the heat absorption is calculated to be about 15,000 calories.

According to the above, it would seem that the energy relations characteristic of the primary photochemical change, which is involved in the combination between hydrogen and chlorine, are entirely obscured by the subsequent secondary changes and, in Nernst's opinion, if the primary change is to be studied under favourable conditions, it is necessary to provide an "acceptor" more suitable than hydrogen for the activated product of the photochemical change. Such acceptors for bromine atoms are said to be furnished by certain hydrocarbons and an investigation⁶² of the rate of combination of hydrogen and bromine in the presence of *cyclohexane* as acceptor has given results which appear to be in very satisfactory agreement with the requirements of the law of photochemical equivalence.

Some interesting facts have been disclosed as a result of the investigation⁶³ of the action of light of definite wave-length on the system $\text{SO}_2 + \text{Cl}_2 \rightleftharpoons \text{SO}_2\text{Cl}_2$. The three substances concerned in this reversible change have absorption spectra in which the maxima are so distributed as to permit of illumination by light

⁶⁰ M. Bodenstein, *Zeitsch. Elektrochem.*, 1913, 19, 836; *A.*, 1913, ii, 1039.

⁶¹ *Ibid.*, 1918, 24, 335; *A.*, ii, 208. ⁶² L. Pusch, *ibid.*, 336; *A.*, ii, 208.

⁶³ M. Le Blanc, K. Andrich, and W. Kangro, *ibid.*, 1919, 25, 229; *A.*, ii, 442.

which is absorbed by one of the substances but not by the other two. When a mixture of sulphur dioxide and chlorine is exposed to light which is absorbed by the sulphur dioxide, there is no formation of sulphuryl chloride, although the presence of the gas mixture falls to a slight extent as the result of a side reaction. If, however, the mixture is acted on by light which is absorbed only by chlorine, reaction takes place until a condition of equilibrium is reached. In this stationary condition the proportion of sulphuryl chloride is greater than in the non-illuminated condition of equilibrium and the displacement due to the radiation factor increases as the temperature is lowered. Illumination of sulphuryl chloride by light which is absorbed by this substance but not to any appreciable extent by sulphur dioxide or chlorine results in the quantitative decomposition of the acid chloride. The observations have obviously an important bearing on the question of the effect of radiant energy on reversible thermal equilibrium and would seem to invite a closer theoretical analysis.

Catalysis in Heterogeneous Systems.

The phenomena comprised under the head of heterogeneous catalysis are now generally attributed to the existence of molecular conditions at the interfacial surface which are sharply differentiated from those obtaining in the liquid or gaseous medium in which the reacting substances are contained. This distinctive character of the interfacial molecular condition forms an essential feature of the theory put forward by Langmuir,⁶⁴ who assumes that the surface of a solid catalyst becomes coated with a single layer of molecules by adsorption of one or other of the reacting substances from the surrounding liquid or gaseous medium. Such condensation is frequently accompanied by a change in the character of the adsorbed molecules and may result in the dissociation of elementary molecules into atoms, the cause of this being found in the localised valencies or lines of force by which the atoms of the condensed substances are definitely associated with certain atoms of the solid in the surface layer. The experimental evidence favourable to Langmuir's hypothesis is not inconsiderable, but it is not proposed to deal with this in the present Report.

W. C. M. Lewis⁶⁵ has made use of Langmuir's theory in an attempt to apply the radiation hypothesis to heterogeneous reactions. According to this hypothesis, the influence of temperature on the velocity of reaction in heterogeneous systems is less than the temperature influence in homogeneous systems because the critical

⁶⁴ I. Langmuir, *loc. cit.*

⁶⁵ *T.*, 1919, 115, 182.

increment in the case of the heterogeneous reaction is less than that which is characteristic of the homogeneous reaction. If the critical increments for the reacting substances are denoted by E_1 (homogeneous reaction) and E_2 (reaction in presence of a solid catalyst), then $E_1 > E_2$ and the ratio of the velocity constants in presence and absence of the catalyst is given, as a first approximation, by $e^{-E_2/RT}/e^{-E_1/RT}$ or $e^{(E_1-E_2)/RT}$. This ratio, which may be termed the catalytic factor, is in general a large positive quantity.

If the reaction in question involves the dissociation of gaseous molecules, the critical increment for the homogeneous reaction may be of the order of 50,000 to 100,000 calories per gram-molecule, and since this energy, on the radiation hypothesis, has to be supplied by absorption of the radiation present in the system, increments of this order must necessarily be associated with high temperatures for the supply of high frequency quanta in sufficient quantities. If, on the other hand, the reaction takes place in the presence of a solid catalyst, on the surface of which the gas is condensed, or adsorbed in the atomic form, the energy corresponding with the critical increment represents the difference between the heat of sublimation or desorption of the atoms and the heat of condensation or adsorption of the molecules. These differences are in general small, say, of the order 5,000 to 10,000 calories per gram-molecule. Taking the lower values for the critical increments, the catalytic factor is given by $e^{(50,000-5,000)/RT}$, and at $T=1,000^\circ$ this is equal to $e^{22.5}$ or 10^{10} . This high value is consonant with the known high efficiency of solid catalysts.

According to the above view, the function of the catalyst is to bring at least one of the reacting substances into an active form for the production of which in a homogeneous gaseous system the requisite high frequency quanta would only be available at exceedingly high temperatures. The lower frequency quanta required in presence of a catalyst are available at much lower temperatures.

Influence of Temperature on Reversible Change.

It has been shown⁶⁶ that the influence of temperature on the equilibrium in reversible reaction systems may be predicted on the basis of the radiation hypothesis and that the result agrees with the well known thermodynamic relation. If $A \rightleftharpoons B$ is a reversible change in which B is formed with the absorption of heat, then, for a given rise in temperature, the relative increase in the density of the radiation which is absorbed by A is greater than the corresponding increase in the density of the radiation absorbed by B .

⁶⁶ W. C. McC. Lewis, *T.*, 1919, 115, 710.

The result is that the velocity of the reaction $A \rightarrow B$ is increased in greater measure than the velocity of the opposed reaction $B \rightarrow A$ and the equilibrium is accordingly displaced in the direction of the endothermic product as required by the Le Chatelier-Braun principle.

Inflammability of Gaseous Mixtures.

The connexion between the lower limits of inflammability of single gases and their mixtures has been submitted to examination in experiments⁶⁷ with hydrogen, methane and carbon monoxide taken two at a time or all three together. The results obtained afford evidence in support of the validity of the formula put forward by Le Chatelier.⁶⁸ This formula, originally limited to binary mixtures of combustible gases, may be written in the form

$$L = 100 / (p_1/L_1 + p_2/L_2 + p_3/L_3 \dots),$$

in which L is the lower limit for a combustible gas mixture in which the percentage proportions of the constituents are $p_1, p_2, p_3 \dots$ and $L_1, L_2, L_3 \dots$ are the lower limits of inflammability for these constituents. The agreement between the observed and calculated values of L for both binary and ternary mixtures is quite satisfactory.

The same formula has been found⁶⁹ to express the connexion between the upper inflammability limits of mixtures of hydrogen, methane and carbon monoxide and those of the constituent gases.

Additive relations of the same kind are shown⁷⁰ to hold for the speed of propagation of flame, which may be calculated from the formula $V = (p_1 + p_2 + p_3 \dots) / (p_1/V_1 + p_2/V_2 + p_3/V_3 + \dots)$ in which V is the speed of propagation for the composite gases and $V_1, V_2, V_3 \dots$ the corresponding speeds of propagation for the constituent gases. For upper- and lower-limit mixtures, in which the speed of propagation is slowest, and also for mixtures in which the speeds are fastest, the agreement between the calculated and observed speeds is as close as can be expected.

The fact that the speed with which flame spreads through an inflammable mixture of gases is dependent in a large measure on the degree of mechanical agitation or turbulence of the mixture has been recognised for some considerable time, and the fundamental importance of the increased rate of explosion under the conditions which obtain in actual gas-engine cylinders, as compared with the

⁶⁷ H. F. Coward, C. W. Carpenter, and W. Payman, *T.*, 1919, 115, 27.

⁶⁸ "Le Carbone," p. 266, Paris, 1908.

⁶⁹ H. F. Coward, C. W. Carpenter, and W. Payman, *T.*, 1919, 115, 31.

⁷⁰ W. Payman and R. V. Wheeler, *ibid.*, 36.

rate in non-turbulent mixtures of the same composition, has been clearly pointed out by Sir D. Clerk.⁷¹

Further observations⁷² made on mixtures of ethane and air near the lower limit of inflammability show that the turbulence of a mixture poor in combustible gas renders it difficult for the flame to spread from the point of ignition and travel through the mixture. When, however, the flame succeeds in spreading from the igniting source, it travels rapidly. As in the case of mixtures richer in combustible gas, the effect of agitation on the rapidity with which the explosion spreads is a purely mechanical one, resulting from the deformation of the flame surface and the rapid multiplication of centres from which further propagation of the flame takes place. In support of this view, it is found that mixtures for which the normal speed of propagation is low are more susceptible to the influence of turbulence than those for which the normal speed is high.

An investigation of the soap-bubble method⁷³ for the determination of ignition-temperatures seems to show⁷⁴ that the values obtained by this method are not nearly so accurate as the results communicated in the original publication would suggest, and that the method, although convenient and rapid in application, is incapable of giving true ignition-temperatures or even of yielding comparative results for different explosive mixtures. The temperatures recorded are apparently dependent on the physical condition of the igniting surface and on the nature of the material of which the electrically-heated igniting coils are made. For a given explosive mixture, the temperatures obtained by using different coils are found to vary by more than 150°, and on the evidence put forward it seems impossible to regard temperatures of ignition determined by the soap-bubble method as trustworthy.

Experiments on the ignition of explosive gases by sparks produced in signal-bell circuits have led to the opinion⁷⁵ that ignition by a rapid break flash depends on the inductance voltage, whereas the igniting power of the flash depends on its energy when the break of the circuit is made slowly. With the object of defining more precisely the property of the spark on which ignition depends, further experiments⁷⁶ with low tension sparks have been made in which the magnetic conditions were varied between wide limits.

⁷¹ Gustave Canet Lecture (Junior Institution of Engineers, 1913).

⁷² R. V. Wheeler, *T.*, 1919, 115, 81.

⁷³ J. W. McDavid, *ibid.*, 1917, 111, 1003. Compare *Ann. Report*, 1917, 22.

⁷⁴ A. G. White and T. W. Price, *ibid.*, 1919, 115, 1248.

⁷⁵ Home Office Report on Electric Signalling with bare Wires, R. V. Wheeler and W. M. Thornton. 1916.

⁷⁶ J. D. Morgan, *T.*, 1919, 115, 94.

The results obtained, when considered in relation to other recent observations, lead to the conclusion that the incendivity of a spark does not depend on its total energy. The fact that increase in the initial intensity of the spark is accompanied by increased incendivity suggests that ignition is mainly dependent on the initial period of the spark discharge and that there is a certain proportion of the total energy which makes no contribution to the process of ignition. If this view is correct, it would follow that the specification of inflammability in terms of the total energy of the least igniting spark is impracticable, and it may be that this is the cause of the divergence of the results which have been obtained in attempts to specify the inflammability of gas mixtures on this basis.

H. M. DAWSON.

INORGANIC CHEMISTRY.

ALTHOUGH it is not possible to report any material increase in the numbers of papers which have been published during the year, yet there is no doubt that much valuable work has been carried out. In general it may be said that the records have a more than common interest. In particular two investigations may be mentioned as being of especial importance. First and foremost is the discovery by Sir Ernest Rutherford that the atom of nitrogen is disintegrated or decomposed when it is bombarded by the α -particles fired off from radium-C. There is no doubt that the shock of the collision is sufficient to disrupt the atom and cause it to decompose into two atoms of hydrogen and possibly three atoms of helium, but the latter has not yet been proved. The fundamental importance of this discovery must be acknowledged by everyone. The great debt that chemistry owes to physicists is still further increased, for it cannot be denied that the influence of the sister science on the fundamental principles of chemistry has been profound. Radioactivity, on the one hand, and the energy quantum theory on the other, exemplify the truth of this. The energy quantum theory is not yet fully weaned, but it bids fair to have as profound an influence on the chemistry of to-day as had John Dalton's theory of material quanta, the atoms, on the chemistry of his day.

A second paper of note is that by Dr. Maxted, on the poisoning of palladium as a catalyst by hydrogen sulphide. For the first time a quantitative basis has been found for the activation of a gas by a catalyst. Although this may by some be thought to lie outside the purview of pure inorganic chemistry, yet this is not a fair criticism. The resolution of hydrogen sulphide into hydrogen and sulphur, and the formation of the complex Pd_4S is pure inorganic chemistry. To mention these facts without reference to the resulting depression of the occlusive power of palladium and the quantitative relation now discovered would be an injustice to this branch of chemistry, which promises to become one of the most fruitful fields of investigation of the problems of chemical reaction.

Atomic Weights.

The International Committee on Atomic Weights has issued a report on the experimental work that has been carried out on atomic weights since 1916. The report deals in particular with the atomic weights of hydrogen, carbon, bromine, boron, fluorine, lead, gallium, zirconium, tin, tellurium, yttrium, samarium, dysprosium, erbium, thorium, uranium, helium, and argon. Attention is drawn to certain important determinations and it is recommended that new values be adopted for the atomic weights of argon, boron, gallium, yttrium, and thorium.

Argon.—From the density and compressibility of this gas Leduc found the atomic weight to be 39.91.¹ Since there is some uncertainty as to the second decimal place the new value 39.9 has been adopted.

Boron.—The atomic weight of boron has been determined by the conversion of anhydrous borax into sodium sulphate, carbonate, nitrate, chloride, and fluoride.² Eight independent values were obtained for boron, ranging from 10.896 to 10.905, and it is recommended that the mean value of 10.90 be adopted.

Gallium.—Some preliminary determinations of the atomic weight of gallium from the analysis of gallium chloride gave the values of 70.09 and 70.11.³ The provisional adoption of 70.10 is recommended.

Thorium.—It is now recommended that the value of 232.15 be adopted for the atomic weight of thorium, based on a series of analyses of thorium bromide.⁴ Two values were obtained, namely, 232.152 from the silver ratio, and 232.150 from the Ag:Cl ratio when Br=79.916.

Yttrium.—The atomic weight of yttrium has been determined from the analysis of the anhydrous chloride.⁵ Seven specimens of this salt were used and the extreme values 89.30 and 89.34 were obtained. It is recommended that the value 89.33 be adopted.

The Committee also recommends that in place of the value of 14.01 for nitrogen the more precise value 14.008 be adopted, which is probably correct to within 1 unit in the third decimal place.

Reference may be made to a determination of the atomic weight

¹ A. Leduc, *Compt. rend.*, 1918, **167**, 70; *A.*, 1918, ii, 266.

² Smith and Van Haagen, *Carnegie Inst. Washington, Publ. No. 267*, 1918.

³ T. W. Richards, W. M. Craig, and J. Sameshima, *J. Amer. Chem. Soc.*, 1919, **41**, 133; *A.*, ii, 158.

⁴ O. Hönigschmid and (Mlle.) S. Horovitz, *Monatsh.*, 1916, **37**, 105; *A.*, 1916, ii, 484.

⁵ H. C. Kremers and B. S. Hopkins, *J. Amer. Chem. Soc.*, 1919, **41**, 716; *A.*, ii, 466.

of scandium by analysis of the bromide.⁶ Two specimens of scandium were employed, both of which were found to be spectroscopically pure. From one the value $Sc=45.105$ was obtained as the mean of eight experiments, whilst the other gave as the mean of ten experiments $Sc=45.093$. The mean of the whole is 45.099 ± 0.014 , which differs considerably from the present international value 44.1. Since the last reference to the subject in the Annual Report for 1916 a considerable amount of work has been carried out on the atomic weights of the isotopes of lead, and several papers have appeared during this year.^{7, 8, 9, 10, 11} It is hardly possible as yet to draw any definite conclusions from this work as to the atomic weights of these isotopes since the values obtained by different experimenters are not concordant. The problem would appear to be complex owing to the possibility that the isotopes themselves are not stable.

Several papers also have been published on the present-day conception of chemical elements, both from the point of view of atomic structure and from the point of view of atomic stability. Amongst the former the most outstanding contribution is a new theory of the atom developed by Langmuir.¹² Although this does not fall within the purview of this Report, yet it cannot be passed by without notice because the new conception would seem to account for the phenomena of valency and chemical combination in a better way than does the Bohr-Rutherford atom.

Then again brief reference must be made to very striking work of Rutherford on the collision of α -particles with light atoms.¹³ The most astonishing result was obtained with nitrogen when submitted to the action of α -particles from radium-C. The results obtained leave little doubt that when a nitrogen molecule collides with an α -particle the result is not nitrogen atoms but atoms of hydrogen or atoms of mass 2. It is interesting to note that whilst the majority of the light atoms have atomic weights represented by $4n$ or $4n+3$, where n is a whole number, nitrogen is the only one with an atomic weight of $4n+2$. Radioactive data would lead

⁶ O. Hönigschmid, *Zeitsch. Elektrochem.*, 1919, **25**, 91; *A.*, ii, 285.

⁷ T. W. Richards and N. F. Hall, *J. Amer. Chem. Soc.*, 1917, **39**, 537; *A.*, 1917, ii, 230.

⁸ A. L. Davis, *J. Physical Chem.*, 1918, **22**, 631; *A.*, ii, 107.

⁹ S. Meyer, *Monatsh.*, 1919, **40**, 1; *A.*, ii, 385.

¹⁰ O. Hönigschmid, *Zeitsch. Elektrochem.*, 1917, **23**, 161; *A.*, ii, 465.

¹¹ K. Fajans, F. Richter, and (Frl.) J. Rauchenberger, *Sitzungsber. Heidelberger Akad. Wiss.*, 1918, 28; *A.*, ii, 7.

¹² I. Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 868; *A.*, ii, 328.

¹³ Sir E. Rutherford, *Phil. Mag.*, 1919, [vi], **37**, 537, 562, 571, 581; *A.*, ii, 256, 258, 259, 260.

to the view that the nitrogen atomic nucleus consists of three helium nuclei and either two hydrogen nuclei or one of mass 2. It is difficult to avoid the conclusion that the nitrogen atom when in collision with an α -particle is disrupted into helium and hydrogen, and Rutherford suggests the probability that the use of α -particles or similar projectiles, of still greater velocity, will result in the disintegration of many of the elementary atoms of small atomic weight.

Although radioactive data, as Rutherford says, may have led to the conclusion that the nucleus of the nitrogen atom is compounded from three helium nuclei and two hydrogen nuclei, yet to the student of inorganic chemistry this observation of its disintegration must form one of the most remarkable of those made in recent years. In his lecture before the Chemical Society Soddy¹⁴ has laid great stress on the far-reaching conclusions as to atomic structure that have been drawn from the study of radioactivity. However definite may be the arguments leading to a specific conclusion, it must be confessed that the conservatism of a chemist will only give way before real experimental proof. It is quite true that the whole question of atomic structure and atomic stability was raised by the discovery of radioactive disintegration, but to many chemists this phenomenon was only a troublesome property of one or two less common elements of large atomic weight. They found security in the statement that the radioactive disintegration of an element is quite independent of external influence, and thus believed the lighter atoms to be perfectly stable entities. In reality it is this independence that has been found to be incorrect, for it has been found possible to induce atomic disintegration by the use of particles moving with great velocity, and the disintegration of nitrogen is the first to be observed.

Molecular Weights.

An important paper has been published on the molecular weight of molten sulphur.¹⁵ The method employed was that of surface-tension measurements made from observations of the rise in capillary tubes. Considerable difficulty was found at first in obtaining pure specimens of sulphur. This was overcome by distilling the sulphur and immediately pouring the distillate into the experimental apparatus. The apparatus was then filled with dry nitrogen and the sulphur boiled for 15 to 20 minutes. After cooling the apparatus was exhausted and allowed to remain overnight. It was then again filled with nitrogen and the sulphur once more boiled. This procedure was generally found sufficient to free the

¹⁴ F. Soddy, *T.*, 1910, 115, 1.

¹⁵ A. M. Kellas, *ibid.*, 1918, 113, 903.

sulphur from all impurities. It was found that a remarkable change in the molecular complexity occurs at about 160° . By the Ramsay and Shields method of calculation the molecule of sulphur between 117° and 157° is found to be S_6 , whilst between 160° and 445° it is S_{18} . It would seem, therefore, that the sulphur molecule undergoes an endothermic termolecular polymerisation at about 160° , $3S_6 = (S_6)_3$. The author draws attention to the various criticisms that have been made of the Ramsay and Shields method and points out that all the recent methods of calculation indicate considerable association. Whilst the complex S_6 for mobile sulphur is corroborated by several methods, yet the Ramsay and Shields values seem to agree better with the experimental results.

In connexion with this work there may be mentioned an investigation into the light-absorbing power of sulphur vapour between the temperature limits of 400° and $1,200^{\circ}$.¹⁶ The remarkable fact is recorded that the absorption of light increases to a maximum at 650° and then decreases with increase of temperature. Moreover, there appears to be a definite absorption band developed, which has a maximum intensity at 650° and decreases rapidly in intensity as the temperature is decreased or increased. It is thus evident that the molecular intensity at 650° must differ markedly from that at 400° and $1,200^{\circ}$. According to Biltz the sulphur vapour at the lower temperature consists of S_8 and at the higher temperature of S_2 molecules. No determinations of the vapour density of sulphur were made by Biltz between 606° and $1,400^{\circ}$, but by extrapolation of his curve the density value for the temperature 650° corresponds with the formula S_3 . It is very noteworthy that this temperature is the very one at which the optical properties of the vapour are distinct from those of the vapour composed of S_8 or S_2 molecules. It is to be remembered that ozone has a greater absorptive power than oxygen. For these reasons the conclusion is drawn that at 650° S_3 molecules form the principal component of the equilibrium in sulphur vapour.

Group I.

Investigation has been made of the normal and acid sulphates of sodium in equilibrium with neutral and acid solutions over the temperature range from -30° to 120° .¹⁷ The existence of the following salts was confirmed: Na_2SO_4 ; $Na_2SO_4 \cdot 7H_2O$; $Na_2SO_4 \cdot 10H_2O$; $Na_2SO_4 \cdot NaHSO_4$; $NaHSO_4$; $NaHSO_4 \cdot H_2O$; $NaHSO_4 \cdot H_2SO_4$; $NaHSO_4 \cdot H_2SO_4 \cdot 1.5H_2O$; $Na_2SO_4 \cdot 2NaHSO_4$.

¹⁶ Sir J. J. Dobbie and J. J. Fox, *Proc. Roy. Soc.*, 1919, [A], **95**, 484; *A.*, ii, 334.

¹⁷ P. Pascal and Ero, *Bull. Soc. chim.*, 1919, [iv], **25**, 35; *A.*, ii, 154.

A similar investigation¹⁸ has been carried out, but under more limited conditions as the observations were made at only two temperatures, 14° and 25°. In addition to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ the following were obtained: Na_2SO_4 , NaHSO_4 , and $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$. In this paper the investigation is described of the systems $\text{CuSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot \text{H}_2\text{O}$, and $\text{Na}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. In the first no acid sulphates of copper were obtained, the effect of the sulphuric acid merely being to dehydrate the pentahydrate in stages to the trihydrate, monohydrate, and the anhydrous salt. In the second series the double salt $\text{Na}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 2\text{H}_2\text{O}$ was obtained above 16·7°, whilst in the third series no salt other than those mentioned was obtained.

Methods have been described for the preparation of the yellow amorphous modification of cuprous oxide.¹⁹ It is most readily obtained by the reduction of a cupric salt by means of hydroxylamine in the presence of alkali. It can also be prepared electrolytically, using an alkali sulphate as the electrolyte and an anode of pure copper. The amorphous oxide when first precipitated is pale yellow and is probably a hydroxide. In the absence of air the colour quickly changes to orange or brick-red, probably through loss of water. After drying, the oxide contains 2—3 per cent. of absorbed water. On heating at a high temperature, above a low red heat, the water is lost and the amorphous oxide changes into the stable red crystalline modification.

By the addition of a slight excess of sodium hydroxide to an aqueous solution of copper and aluminium sulphates containing approximately 5 per cent. of CuO and 95 per cent. of Al_2O_3 , a very pale blue precipitate is obtained.²⁰ This precipitate retains its colour after being thoroughly washed and dried at 100°. When ground to a very fine powder and heated, first in a Bunsen flame and then in a blowpipe flame, it changes in colour to a pale greyish-blue with no signs of blackening. If the precipitate contains about twice as much cupric oxide it remains blue after heating in the Bunsen flame, but shows signs of blackening when heated in the blowpipe flame. It is suggested that the alumina stabilises the blue cupric oxide and that the change from blue to black is due to an agglomeration of the particles. Analogous results were obtained in some preliminary experiments with manganous, cobaltous, and nickelous oxides.

¹⁸ H. W. Foote, *J. Ind. Eng. Chem.*, 1919, **11**, 629; *A.*, ii, 361.

¹⁹ L. Moser, *Zeitsch. anorg. Chem.*, 1919, **105**, 112; *A.*, ii, 155.

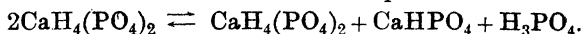
²⁰ H. E. Schenck, *J. Physical Chem.*, 1919, **23**, 283; *A.*, ii, 286.

Group II.

A convenient method has been described for the extraction of glucinum from beryl.²¹ The powdered mineral is treated with two parts of sodium silicofluoride at 850° for 30 to 40 minutes. The silicon fluoride which is evolved at this temperature attacks the beryl and forms glucinum fluoride and aluminium fluoride, which in turn combine with the sodium fluoride to give the corresponding double fluorides. On extracting the material with boiling water, the sodium glucinum fluoride dissolves, and the filtrate contains practically the whole of the glucinum together with a little alumina and silica. A slight excess of boiling sodium hydroxide solution is added, and the precipitated oxides are collected and redissolved in sulphuric acid. The solution is concentrated and the glucinum sulphate is allowed to crystallise. By this method 90 per cent. of the glucinum present in the mineral may be readily recovered. Based on this process a method is described for the estimation of glucinum in beryl.

It has been found that alloys of magnesium and lead containing from 5 to 50 per cent. of magnesium are very reactive, and when exposed to moist air readily absorb the whole of the oxygen present.²² The two metals form the compound Mg_2Pb and this alloy, containing 90 per cent. of magnesium, is the most reactive of the series. During the oxidation process the alloy crumbles to a black powder which consists of magnesium hydroxide, $Mg(OH)_2$, and hydrated lead sub-oxide, $Pb_2(OH)_2$. In dry air the mixture may be kept unchanged, but in the presence of water the lead sub-oxide is oxidised to $Pb(OH)_2$. With the more reactive alloys, the action takes place in the cold, but when more than 35 per cent. of magnesium is present heat is necessary. Alloys of magnesium and zinc are far less reactive, and indeed show greater resistance to oxidation than either magnesium or zinc.

A scientific investigation of commercial superphosphates has been described and although the principal subject involved is the question of the preparation and analysis, the results are of importance in connexion with monocalcium phosphate and dicalcium phosphate.²³ When increasing quantities of monocalcium phosphate are dissolved in a given weight of water at constant temperature, the proportion of free phosphoric acid continually increases and tends towards a limit in accordance with the equation

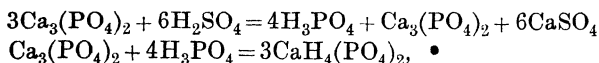


²¹ H. Copaux, *Compt. rend.*, 1919, **168**, 610; *A.*, ii, 192.

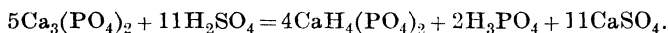
²² E. A. Ashcroft, *Trans. Faraday Soc.*, 1919, **14**, 271; *A.*, ii, 465.

²³ A. Aita, *Annali Chim. Appl.*, 1918, **10**, 45; *A.*, ii, 25.

Up to the saturation point at 15° there thus exists a liquid phase consisting of water, monocalcium phosphate, and free phosphoric acid, and a solid phase of dicalcium phosphate formed by hydrolysis of the monocalcium phosphate. It is commonly believed that the reaction between sulphuric acid and mineral phosphates takes place in two stages:—



but it would seem that the principal reaction is more correctly represented by the equation:



The influence of raising the temperature on the reaction is to increase the concentration of phosphoric acid in the liquid phase, whilst in the solid phase dicalcium phosphate increases in equal proportion with the free phosphoric acid. These constituents gradually react to form monocalcium phosphates.

An investigation has been made of the decomposition of barium peroxide by heat at atmospheric pressure, the method being that of the observation of the heating curve.²⁴ The peroxide was heated in a carbon tube furnace and the temperature was recorded every 10 seconds. Since the decomposition is an endothermic reaction its temperature range is indicated by a pronounced flattening of the curve towards the time axis. The temperature at which the dissociation pressure is equal to 760 mm. was found to be 795°, which is in good agreement with Le Chatelier's value 796°.

In the presence of cupric oxide barium peroxide starts to decompose at 200°, the reaction becoming most vigorous at 625° to 660°. On the other hand, when the peroxide is heated with amorphous silica the rate of rise of temperature is increased above 400°. In all probability this is due to an exothermic reaction between the barium oxide and silica to give barium silicate. The heating curve shows a similar indication of the formation of silicate even when the peroxide has been mixed with powdered quartz glass or quartz.

In connexion with this it may be noted that strontium peroxide may be prepared from strontium oxide by heating it in oxygen under a pressure of 105 to 126 kilos. per sq. cm. at a temperature of 400° to 500°.²⁵ The product contains more than 85 per cent. of SrO_2 and resembles barium peroxide in its physical properties.

The preparation of various sub-oxides of cadmium has been described from time to time and the previous investigations have

²⁴ J. A. Hedvall, *Zeitsch. anorg. Chem.*, 1918, **104**, 163; *A.*, ii, 26.

²⁵ J. B. Pierce, jun., *Brit. Pat.* 130840; *A.*, ii, 413.

now been repeated.²⁶ The first method consisted in heating the oxalate at 300° in a rapid stream of carbon dioxide. A small quantity of green material was obtained which, however, contained free cadmium. Analysis of this heterogeneous material gave values closely approximating to $\text{Cd} = 96.5$ per cent., whilst Cd_4O ²⁷ requires 96.56 per cent. By heating this substance in a vacuum it was found possible to distil off the free cadmium, leaving a homogeneous green mass which on analysis was found to be Cd_2O .

The reduction of the brown oxide in hydrogen or carbon monoxide always gave an obvious mixture of the oxide and cadmium. The process described by Morse and Jones²⁸ was repeated and small quantities of Cd_2O were obtained. Anhydrous cadmium chloride is fused with cadmium and the product treated with water. Cadmious hydroxide is obtained from which yellow cadmium sub-oxide may readily be prepared by dehydration. By each of these processes Cd_2O may be prepared, but only in very small quantities.

Anhydrous mercuric fluoride has been obtained by heating mercurous fluoride in a current of dry chlorine at 275°, or of dry bromine at 400°.²⁹ It may also be prepared by heating mercurous fluoride at 450° under 10 mm. pressure. It forms transparent, octahedral crystals, m.p. 645° and b.p. estimated at 650°. The vapour of mercuric fluoride is very reactive, and therefore it was not found possible to measure its vapour pressure at various temperatures since the containing vessels are attacked. The substance reacts very readily with moisture and becomes discoloured in the presence of minute traces of water vapour. On exposure to moist air, hydrogen fluoride is evolved and mercuric oxyfluoride and, ultimately, mercuric oxide are formed. With small quantities of water, a white, hydrated oxyfluoride, $\text{Hg}_3\text{F}_4(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, is produced. By cautious evaporation of a solution of mercuric fluoride in a 40 per cent. solution of hydrogen fluoride small colourless crystals are deposited of the hydrated fluoride, $\text{HgF}_2 \cdot 2\text{H}_2\text{O}$.

Mixtures of the anhydrous fluoride with silver, copper, lead, aluminium, magnesium, zinc, tin, chromium, iron, or arsenic react vigorously when strongly heated, yielding amalgams and metallic fluorides. The latter may readily be isolated in the pure condition if an excess of mercuric fluoride be used. Silicon fluoride appears to be formed when mercuric fluoride is heated with silicon, but no reaction occurs with either amorphous or graphitic carbon.

²⁶ H. G. Denham, *T.*, 1919, **115**, 556.

²⁷ S. Tanatar, *Zeitsch. anorg. Chem.*, 1901, **27**, 432; *A.*, 1901, ii, 553.

²⁸ H. N. Morse and H. C. Jones, *Amer. Chem. J.*, 1890, **12**, 488; *A.*, 1890, 1376.

²⁹ O. Ruff and G. Bahlau, *Ber.*, 1918, **51**, 1752; *A.*, ii, 65.

By heating mercurous fluoride in a current of dry chlorine at 120° mercuric chlorofluoride is formed, and similarly the bromofluoride is obtained at 105° . Both these substances are pale yellow.

By the action of various thioamides on mercuric nitrite a complex sulphoxynitrite of mercury has been prepared.³⁰ This compound is heavy, granular, and yellow, and can be dried in a steam-oven. By analysis the empirical formula was found to be $3(\text{SHgNO}_2), \text{HgO}$, but it is suggested that the molecular formula is $[3(\text{SHgNO}_2), \text{HgO}]_2$, since the unimolecular formula represents an unsaturated compound. This substance is insoluble in water or acetone, but dissolves in hydrochloric acid with copious evolution of nitrous fumes. When boiled with water it decomposes and is converted into black mercuric sulphide. In a similar manner the compound $(\text{SHgNO}_2)_2\text{O}$ has been obtained. By the action of ethyl iodide on the sulphoxynitrite dimercuric di-iododisulphide, $\text{I} \cdot \text{Hg} \cdot \text{S} \cdot \text{S} \cdot \text{Hg} \cdot \text{I}$, is produced. This compound is a pale yellow granular powder which darkens in the light, but regains its colour when kept in the dark.

The chlorine analogue of the sulphoxynitrite, $[3(\text{SHgCl}), \text{HgO}]_2$, has also been prepared by the action of certain thioamides on mercuric chloride.³¹ It forms a white amorphous precipitate which on remaining for 24 hours becomes granular.

Group III.

Some very interesting work has been carried out on the separation and purification of gallium.³² In the first place, a method has been described for the recovery of gallium and also of germanium from zinc ores. Since both these metals are less volatile than zinc they remain behind in the retorts when the zinc distils off. These residues furnish a good source of gallium and germanium, although the amounts obtainable vary very considerably. The method of treatment may be very briefly described. One kilo. of the oxide prepared from the zinc residues was added in small portions at a time to 2400 c.c. of hydrochloric acid. When all had dissolved a little potassium chlorate was added carefully until, after vigorous shaking, oxides of chlorine were evolved. The solution was then distilled with a thermometer placed with its bulb in the liquid. Two fractions were collected, the first, up to 121° , containing very little germanium, and the second, up to $135\text{--}140^{\circ}$, containing practically the whole of the germanium. The second fractions from

³⁰ P. C. Rây, *T.*, 1917, 111, 101.

³¹ Sir P. C. Rây and P. K. Sen, *ibid.*, 1919, 115, 552.

³² H. C. Fogg and C. James, *J. Amer. Chem. Soc.*, 1919, 41, 947; *A.*, ii, 344.

several quantities were saturated with hydrogen sulphide and the white germanium sulphide filtered off. The liquid left in the flask was diluted in water and the lead chloride allowed to settle. The clear liquid was decanted and treated with ammonium hydroxide until a slight permanent precipitate was obtained, metallic zinc was added, and the whole digested at the boiling point for several hours, after which the precipitated metals and basic salts were collected. Ten such precipitates were united and dissolved in hydrochloric acid with the aid of a little potassium chlorate and the lead chloride allowed to settle. The clear liquid was again saturated with hydrogen sulphide and filtered. The filtrate was boiled, neutralised with ammonium hydroxide until a permanent precipitate was formed, and again digested with zinc at the boiling point. The precipitates rich in gallium were again dissolved in hydrochloric acid, the solution nearly neutralised, saturated with hydrogen sulphide and filtered. The filtrate was treated with ammonium chloride, made alkaline with ammonium hydroxide, and boiled until just acid. A gelatinous precipitate consisting of gallium, aluminium, and iron hydroxides was filtered off and washed. The gallium was finally separated from the aluminium by the electrolysis of a strongly alkaline solution of the hydroxides.

Independent work on the preparation of pure gallium and its salts has also been carried out.^{33, 34, 35} In such work the methods of testing the purity are of importance, especially in view of the difficulty of separating gallium from indium. A very delicate test has been found in the spark spectrum, for by this means it is possible to detect as little as 0.06 per cent. of indium in gallium and of 0.18 per cent. of gallium in indium.

It is possible to separate gallium and indium by the electrolysis of a dilute solution of their sulphates, perfectly pure gallium being obtained after 14 electrolyses. Pure gallium chloride can also be obtained from mixtures of gallium, indium, and zinc by the fractional distillations of the chloride in a current of chlorine. A method is described for the separation of gallium and indium by precipitation of their hydroxides. Solutions containing both elements are largely diluted and treated with a little hydrochloric acid, and then exactly neutralised with sodium hydroxide, an excess of 1.5 grams of sodium hydroxide is added and the solution boiled for several minutes. The precipitated indium hydroxide is well washed, dissolved in hydrochloric acid, and the process re-

³³ L. M. Dennis and J. A. Bridgman, *J. Amer. Chem. Soc.*, 1918, **40**, 1531 ; *A.*, 1918, ii, 456.

³⁴ T. W. Richards, W. M. Craig, and J. Sameshima, *ibid.*, 1919, **41**, 131 ; *A.*, ii, 157.

³⁵ T. W. Richards and S. Boyer, *ibid.*, 1933 ; *A.*, ii, 158.

peated. Finally, it is dissolved again in hydrochloric acid, precipitated by ammonia, washed, dried, and ignited to oxide. To the combined filtrates and washings from all these operations sodium sulphite is added, and the solution boiled vigorously for four minutes, when gallium hydroxide is precipitated.

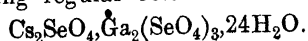
It would seem, however, that the hydroxide separation method is not very satisfactory, since the gallium thus obtained still contains some indium. If, however, the gallium hydroxide is dissolved in an acid and the slightly acid solution electrolysed the gallium is obtained pure. The melting point of the gallium prepared in this way is 30.8° as compared with 26.9° for the metal purified by the hydroxide process.

The compressibility of gallium has been determined and for the solid element is 2.09×10^{-6} , a value which places gallium precisely on the curve showing the periodic relation of this property to atomic weight. The compressibility of liquid gallium is 3.97×10^{-6} , a value almost identical with that of mercury, and nearly twice as great as that of solid gallium, although its volume is less. The densities of solid and liquid gallium are 5.885 and 6.081 respectively, and thus the view that the marked expansion of gallium on solidification is due to impurities is definitely negatived.

In order to obtain pure gallium chloride it is advisable to burn gallium in pure dry chlorine and to distil the impure chloride in pure chlorine, in nitrogen, and in a vacuum successively. This treatment was found necessary to eliminate the dissolved chlorine. A preliminary determination of the atomic weight of gallium has been made by the analysis of pure specimens of the chloride. Reference to this has already been made under Atomic Weights.

Gallium selenate has been prepared by placing gallium hydroxide in less than the equivalent quantity of selenic acid and heating the mixture nearly to the boiling point. After several hours the solution was filtered from the excess of gallium hydroxide and allowed to evaporate at ordinary temperature. The crystals were collected and dried to constant weight in the air, and on analysis were found to have the formula $\text{Ga}_2(\text{SeO}_4)_3 \cdot 16\text{H}_2\text{O}$. It would appear, however, that the crystals which separate from the solution have 22 molecules of water of crystallisation. Gallium sulphate also first crystallises from its solution with 22 molecules of water of crystallisation.

Cæsium gallium selenate alum has been prepared by the evaporation at ordinary temperature of a solution containing cæsium selenate, gallium selenate, and some free selenic acid. This salt is a typical alum, forming regular octahedra with the formula:



The solubilities of ammonium gallium sulphate alum and caesium gallium sulphate alum have been determined, in water and in 50 per cent. and 70 per cent. alcohol, with the view of testing the possibility of using the former salt as a means of separation of gallium. One part of the ammonium alum dissolves in 3.24 parts of water, 4600 parts of 50 per cent. alcohol, and 11,400 parts of 70 per cent. alcohol. One part of the caesium alum dissolves in 66.2 parts of water, 25,800 parts of 50 per cent. alcohol, and 28,000 parts of 70 per cent. alcohol.

Group IV.

The view has been put forward that all varieties of graphite and amorphous carbon are different physical forms of "black carbon," which is to be regarded as an allotropic modification of diamond.^{36, 37} The physical and chemical properties of graphite vary within such wide limits that no distinct line of demarcation can be drawn between graphite and amorphous carbon or soot. The properties of different samples of graphite depend upon the conditions under which it has been produced, and its variable character is to be attributed to different degrees of dispersity. The reactions by which graphite is formed are all of the localised type which have been grouped together under the name of "topochemical" reactions.³⁸ This view is borne out by the X-ray spectra of graphite and amorphous carbon, which lead to the conclusion that the two varieties are identical in structure, and that amorphous carbon differs from graphite only by its greater degree of sub-division.³⁹ In graphite the carbon atoms are arranged hexagonally in plane layers which are superimposed on one another, and as a result graphite owes its peculiar properties to its lamellar structure.

In order further to elucidate the structure of graphite the oxidation of graphite to graphitic acid and the properties of the latter have been studied. In order to guard against any possible variations due to differences in the properties of the samples of graphite, the experiments were confined to a specially pure electrically prepared graphite free from ash. The oxidations were carried out with a mixture of potassium chlorate, nitric acid, and sulphuric acid in the cold under fixed conditions. This mixture is peculiarly

³⁶ V. Kohlschütter, *Zeitsch. anorg. Chem.*, 1919, **105**, 35; *A.*, ii, 151.

³⁷ V. Kohlschütter and P. Haenni, *ibid.*, 121; *A.*, ii, 152.

³⁸ V. Kohlschütter, *ibid.*, 1; *A.*, ii, 156.

³⁹ P. Debye and P. Scherrer, *Physikal. Zeitsch.*, 1917, **18**, 291; *A.*, 1917, ii, 427.

advantageous because it penetrates the whole mass of the graphite. Other oxidising agents which do not penetrate the graphite have little action or oxidise it completely to carbon dioxide. Repeated treatment of the graphitic acid with the oxidising mixture changes its colour from green to brown or yellow, whilst the carbon content gradually diminishes. After five oxidations the graphitic acid has the composition $C=54.4$, $H=2.14$, $O=43.46$ per cent. After repeated washings with water, the graphitic acid passes into solution. The colloid can be precipitated by dilute acids and the gel is perfectly soluble in water. The differently coloured graphitic acids merely differ in their degree of dispersity, the paler coloured products obtained by repeated oxidation being more highly dispersed. When heated or treated with reducing agents graphitic acid is reduced to carbon. The temperature at which the decomposition is explosive is lower the slower the heating, but if the heating is very slow the decomposition may proceed quietly to completion without explosion. The black voluminous residue consists of carbon and has all the properties of soot, but it can be compressed into a mass very similar to graphite. When the decomposition by heat takes place under pressure, the graphitic character of the residual carbon is more marked. Treatment of graphitic acid with reducing agents, such as ferrous or stannous salts, furnishes products with strongly marked graphitic properties giving graphitic acid again when oxidised. These results are considered to support the theory that graphite and amorphous carbon are not different allotropes, but varieties of one allotrope, black carbon.

When carbonyl sulphide⁴⁰ is passed through an electrically heated tube, packed with quartz splinters, it decomposes to give carbon monoxide and sulphur on the one hand, and carbon dioxide and carbon disulphide on the other. Since it has been proved that the two reactions are independent of one another it is probable that the two reactions may be written $2COS \rightleftharpoons 2CO + S_2$ and $2COS \rightleftharpoons CO_2 + CS_2$. Some further experiments have shown that the action of heat on mixtures of carbon monoxide and carbon disulphide on the one hand and carbon monoxide and sulphur on the other, gives the same products as when carbonyl sulphide is heated. The reactions therefore are reversible and true cases of equilibrium exist. Similarly the combustion of carbon disulphide with an insufficient amount of oxygen or of oxygen in carbon disulphide vapour yields a mixture of unchanged carbon disulphide, carbon dioxide, sulphur dioxide, carbonyl sulphide, and carbon monoxide.

⁴⁰ A. Stock and P. Seelig, *Ber.*, 1919, 52, [B], 681; *A.*, ii, 230.

Carbonyl chloride may be prepared by the action of carbon tetrachloride on fuming or ordinary sulphuric acid.^{41, 42} With pyrosulphuric acid the reaction is $\text{SO}_3 + \text{H}_2\text{SO}_4 + \text{CCl}_4 = \text{COCl}_2 + 2\text{SO}_3\text{HCl}$. With ordinary sulphuric acid in the presence of infusorial earth as a catalyst the reaction is $2\text{H}_2\text{SO}_4 + 3\text{CCl}_4 = 3\text{COCl}_2 + \text{HCl} + \text{S}_2\text{O}_5\text{Cl}$ and at 150° without catalyst $\text{CCl}_4 + \text{H}_2\text{SO}_4 = \text{SO}_3\text{HCl} + \text{HCl} + \text{COCl}_2$. If slightly aqueous acid is used the chlorosulphonic acid gives sulphuric acid and hydrochloric acid. The carbonyl chloride is purified by solution in carbon tetrachloride and subsequent distillation.

The sub-acetate and the sub-sulphate of lead⁴³ have been prepared by methods analogous to those used for the sub-haloid salts of this metal.⁴⁴ The sub-acetate was obtained by the action of the vapour of acetic anhydride on the sub-oxide at 195° , whilst the sub-sulphate was formed by the action of methyl sulphate vapour on the sub-oxide at 280° . The latter salt decomposes on solution in water, but is stable to the action of heat, for no sign of any change could be observed on heating it at 440° .

A double nitrate and hypophosphite of lead has been described.⁴⁵ It is obtained by adding, with stirring, pure crystalline lead hypophosphite (250 grams) to a boiling solution of lead nitrate (500 grams) in water (1.5 litres). The mixture is then rapidly cooled when the double salt separates out. It has the formula $\text{Pb}(\text{NO}_3)_2 \cdot \text{Pb}(\text{H}_2\text{PO}_2)_2$ and is explosive. Its use in percussion fuses is recommended.

Some further work on zirconium compounds may be reported.⁴⁶ The basic compounds formed by the hydrolysis of zirconium sulphate in aqueous solution are much more complex than has been supposed and three basic sulphates have been isolated in the crystalline form. In spite of the crystalline character of these compounds their solutions are essentially colloidal. The following basic sulphates have been prepared: $\text{Zr}_4(\text{SO}_4)_3(\text{OH})_{10} \cdot 10\text{H}_2\text{O}$, $\text{Zr}_8(\text{SO}_4)_5(\text{OH})_{22} \cdot 8\text{H}_2\text{O}$, and $[\text{Zr}_4(\text{SO}_4)_6(\text{OH})_8]\text{H}_4 \cdot 4\text{H}_2\text{O}$. The last named had previously been described and given the formula $2\text{ZrO}_2 \cdot 3\text{SO}_3 \cdot 5\text{H}_2\text{O}$, but the new formula takes into account its acid properties and explains its ready conversion into either of the first two compounds. The usually accepted formula for potassium zirconyl sulphate, $\text{Zr}_2\text{O}_3(\text{SO}_4)_2 \cdot \text{K}_2$, is now shown to be incorrect and

⁴¹ V. Grignard and E. Urbain, *Compt. rend.*, 1919, **169**, 17; *A.*, ii, 340.

⁴² C. Mauguin and L. J. Simon, *ibid.*, 34; *A.*, ii, 341.

⁴³ H. G. Denham, *T.*, 1919, **115**, 109.

⁴⁴ *Ibid.*, 1917, **111**, 29; 1918, **113**, 249.

⁴⁵ E. von Herz, *Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1916, **11**, 365, 388; *A.*, ii, 284.

⁴⁶ O. Hauser and H. Herzfeld, *Zeitsch. anorg. Chem.*, 1919, **106**, 1; *A.*, ii, 290.

a definite salt, $\text{Zr}_4(\text{SO}_4)_5(\text{OH})_8\text{K}_2$, has been prepared. The ammonium salt of the above zirconylsulphuric acid, $(\text{NH}_4)_4\text{Zr}_4(\text{OH})_8(\text{SO}_4)_6 \cdot 4\text{H}_2\text{O}$, has been obtained, together with a less basic salt, $(\text{NH}_4)_4\text{Zr}(\text{SO}_4)_4 \cdot 5\text{H}_2\text{O}$. A basic salt, $\text{K}_4[\text{Zr}_4(\text{OH})_8(\text{SO}_4)_5]8\text{H}_2\text{O}$, has also been prepared.

Group V.

Reference was made in the Annual Reports for 1912 and 1915 to Franklin's work on the ammonia system of acids, bases, and salts. A further contribution has been made during this year and certain new compounds have been described.⁴⁷ Dipotassium ammonosodiate, $[\text{Na}(\text{NH}_2)_3]\text{K}_2$, is obtained by the action of potassamide on sodamide in liquid ammonia, by the action of sodium iodide on an excess of potassamide in liquid ammonia, or by the action of sodium on potassamide in liquid ammonia in the presence of a small quantity of platinum black. This compound crystallises well, and does not lose ammonia at 100° in a vacuum. Monorubidium ammonosodiate, $[\text{Na}(\text{NH}_2)_2]\text{Rb}$, is formed by the action of sodium and rubidium simultaneously on liquid ammonia. This compound is readily soluble in liquid ammonia, and is violently decomposed by water with the formation of the hydroxides of the metals. Dirubidium ammonosodiate, $[\text{Na}(\text{NH}_2)_3]\text{Rb}_2$, is formed from the mother liquors of the previous compound by the addition of a large excess of rubidamide. Dipotassium ammonolithiate, $[\text{Li}(\text{NH}_2)_3]\text{K}_2$, is prepared by the action of potassamide on lithium iodide in liquid ammonia solution, and also by the action of lithium and potassium simultaneously on liquid ammonia in the presence of platinum black. Monorubidium ammonolithiate, $[\text{Li}(\text{NH}_2)_2]\text{Rb}$, is prepared by the action of an excess of a solution of rubidamide in liquid ammonia on metallic lithium in the presence of platinum black.

An important investigation has been carried out on the densities of liquid nitrogen peroxide and mixtures of nitrogen peroxide and nitric acid.⁴⁸ The specific volume of nitrogen peroxide between 4° and 18° is expressed by $v = 0.67027 + 0.0010075t + 0.000003t^2$. The boiling point of the liquid is $21.9 \pm 0.1^\circ$. Nitrogen peroxide is soluble in nitric acid up to about 54 per cent. and nitric acid is much less soluble in nitrogen peroxide, about 7 per cent. Within these limits the densities of mixtures of the two substances have been determined at 4° , 11° , and 18° . A maximum density is obtained with the mixture containing about 44 per cent. of nitrogen

⁴⁷ E. C. Franklin, *J. Physical Chem.*, 1919, **23**, 36; *A.*, ii, 191.

⁴⁸ W. R. Bousfield, *T.*, 1919, **115**, 45.

peroxide. On the other hand, the maximum contraction on mixing is found with mixtures containing 49.3 per cent. of nitrogen peroxide. There is considerable heat evolved on mixing which indicates a powerful combination between the two substances. The compound $3\text{HNO}_3, 2\text{N}_2\text{O}_4$ corresponds with 49.33 per cent. of N_2O_4 . The maximum value of the density does not indicate the exact composition of the compound since it is so largely determined by the mere density differences of the two components. When the temperature coefficients of expansion are examined these are found to show a definite minimum for the mixture containing 26.7 per cent. of N_2O_4 , which corresponds with the definite composition $4\text{HNO}_3, \text{N}_2\text{O}_4$. It may therefore be concluded that two specific compounds exist, namely, $3\text{HNO}_3, 2\text{N}_2\text{O}_4$, and $4\text{HNO}_3, \text{N}_2\text{O}_4$.

The maximum density of the solution containing about 43 per cent. of N_2O_4 has been independently observed,⁴⁹ and the authors consider that this gives evidence of the existence of the compound $2\text{HNO}_3, \text{N}_2\text{O}_4$ or $\text{N}_2\text{O}_5, \text{N}_2\text{O}_4, \text{H}_2\text{O}$. They state that the existence of this compound is confirmed by a thermal study of the reciprocal solubilities of nitric acid and nitrogen peroxide. The compound is stable below -48.5° , and at this temperature it dissociates, liberating nitrogen peroxide. The density of nitrogen peroxide is expressed by $D_t = 1.490 - 0.00215t$.

It has generally been believed that the combustion of ammonia in a deficiency of oxygen proceeds according to the equation $4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$. It has, however, been shown that under these conditions the resulting gas consists of about 59 per cent. of nitrogen and 41 per cent. of hydrogen,⁵⁰ the explanation being offered that a portion of the ammonia is dissociated into nitrogen and hydrogen at the high temperature of the flame. If this were the correct explanation considerable quantities of nitrogen should be formed when ammonia is burnt in excess of oxygen, which is not the case. A possible explanation may be found in the formation of the hypothetical di-imide, when insufficient oxygen is present, which would decompose into nitrogen and hydrogen.⁵¹ The reaction may be expressed therefore by the equation $2\text{NH}_3 + \text{O}_2 = \text{N}_2\text{H}_2 + 2\text{H}_2\text{O}$. When potassium hydrazinesulphonate was heated with potassium hydroxide in the expectation that the hydroxyhydrazine primarily formed would immediately give di-imide by loss of water, the calculated amount of potassium sulphite was obtained and a mixture of equal volumes of hydrogen and nitrogen. A second

⁴⁹ P. Pascal and M. Garnier, *Bull. Soc. chim.*, 1919, [iv], 25, 309; A., ii, 339.

⁵⁰ Müller, *Zeitsch. physikal. Chem. Unterr.*, 1913, 163.

⁵¹ F. Raschig, *ibid.*, 1918, 31, 138; A., ii, 149.

alternative is that the combustion proceeds with the intermediate formation of hydrazine, $4\text{NH}_3 + \text{O}_2 = 2\text{N}_2\text{H}_4 + 2\text{H}_2\text{O}$. The formation of hydrazine when oxygen burns in ammonia has actually been proved by the formation of benzylideneazine. It is concluded that the combustion gives mainly di-imide and also hydrazine to a less extent, and that the direct formation of the nitrogen according to the commonly accepted reaction does not take place at all.

The reduction of arsenious acid by means of stannous chloride has been the subject of systematic study.⁵² It was recorded by Bettendorf⁵³ that a voluminous, brown precipitate of arsenic is obtained, accompanied by traces of non-removable tin. There seems little doubt that as the first product of this reaction arsenic is obtained as the yellow allotropic modification. A portion of it is soluble in carbon disulphide and the yield of yellow arsenic is increased if the reaction mixture is shaken with carbon disulphide during the process of reduction. The results indicate that the very earliest deposit of arsenic is of the yellow type, but that unless certain unascertained conditions obtain, the yellow variety spontaneously becomes brown or grey.

The reaction does not take place if the two chlorides are anhydrous, but readily proceeds if the mixture of anhydrous chlorides is moistened with water. In general it is found that the reaction is accelerated chiefly by increase in the concentration of hydrochloric acid, next by that of arsenic chloride, and least by that of stannous chloride. The results obtained in velocity measurements lead to the view that the reaction takes place between arsenious and chloride ions and the complex H_2SnCl_4 . Dilution with water rapidly decreases the velocity, owing no doubt to the hydrolysis of the arsenious chloride.

A number of double compounds have been described of arsenious oxide and the iodides of bivalent light and heavy metals.⁵⁴ The moderately concentrated solution of the iodide is saturated in the hot with arsenious oxide and allowed to cool, when the compound separates in crystals, sometimes with a little free arsenious oxide. The following have been prepared: $\text{GII}_2, 3\text{As}_2\text{O}_3, 8\text{H}_2\text{O}$; $\text{Mg}(\text{or Ca or Sr})\text{I}_2, 3\text{As}_2\text{O}_3, 12\text{H}_2\text{O}$; $\text{BaI}_2, 3\text{As}_2\text{O}_3, 9\text{H}_2\text{O}$; $\text{ZnI}_2, 3\text{As}_2\text{O}_3, 10\text{H}_2\text{O}$; $\text{Mn}(\text{or Fe or Co})\text{I}_2, 4\text{As}_2\text{O}_3, 12\text{H}_2\text{O}$; $\text{NiI}_2, 4\text{As}_2\text{O}_3, 10\text{H}_2\text{O}$; $\text{AlI}_3, 6\text{As}_2\text{O}_3, 18(?)\text{H}_2\text{O}$; $\text{LiI}, 2\text{As}_2\text{O}_3, 3\text{H}_2\text{O}$. In properties these compounds resemble the arsenites of the metals, the characters of the iodides being suppressed. They are moderately stable in dry air, but tend to become oxidised on keeping. With the exception of

⁵² R. G. Durrant, *T.*, 1919, 115, 134.

⁵³ *Sitzungsber. Niederrhein. Ges. Bonn*, 1869, 128.

⁵⁴ R. F. Weinland and P. Gruhl, *Arch. Pharm.*, 1917, 255, 467; *A.*, ii, 411.

the magnesium compound these salts are sparingly soluble in water, and when heated with water they tend to undergo partial dissociation into the iodide and arsenious oxide. It is believed that these compounds approximate in constitution to a complex salt with simple metallic cation.

Investigation has shown that antimony pentoxide does not form the definite hydrates, ortho-, pyro-, and meta-antimonic acids, as has hitherto been supposed.⁵⁵ Analyses of the various hydrates have been made, and their dehydration curves obtained by keeping them over sulphuric acid in a desiccator. It is found that the properties of the antimonic acids vary with the method of preparation and with previous treatment. Thus the modifications prepared either by the action of water on antimony pentachloride or by the action of acids on antimonates, or by the hydrolysis of antimony trichloride in the presence of nitric acid differ in their water content, stability, solubility, and their action towards acids and alkalis. The differences observed are in all probability due to variations in the size of the particles. It appears that the soluble antimonic acids are hydrosols with small stability and that the definite hydrates, H_3SbO_4 , $\text{H}_4\text{Sb}_2\text{O}_7$, and HSbO_3 , can have no free existence. The hydrates exhibit marked selective absorption towards dilute alkalis to give amorphous substances which apparently are alkali antimonates. The hydrates dissolve in concentrated alkali solutions and from these solutions by cautious evaporation at low temperature various alkali antimonates may be crystallised. The nature of these salts depends, however, on the concentration of the mother liquor.

When magnesium which has been covered with thorium-C (an isotope of bismuth) is dissolved in hydrochloric acid, a small quantity of a radioactive hydride is obtained. This observation leads to the belief that bismuth forms a volatile hydride, and the existence of this compound has been definitely proved both by radioactive methods and also by its preparation from non-radioactive materials.^{56, 57} The second method has a greater importance since all criticism arising from possible misconception of radioactive phenomena is eliminated. A bismuth magnesium alloy is prepared by melting together equal weights of powdered bismuth and magnesium (as free from silicon as possible) in an iron crucible in a rapid current of hydrogen. When this alloy is dissolved in approximately 4*N*-hydrochloric or sulphuric acid sufficient bismuth hydride is ob-

⁵⁵ G. Jander, *Kolloid Zeitsch.*, 1918, **23**, 122; *A.*, ii, 29.

⁵⁶ F. Paneth, *Zeitsch. Elektrochem.*, 1918, **24**, 298; *A.*, ii, 30; *Ber.*, 1918, **51**, 1704; *A.*, ii, 67.

⁵⁷ F. Paneth and E. Winternitz, *Ber.*, 1918, **51**, 1728; *A.*, ii, 68.

tained to permit its detection either by the bismuth mirror test or by the luminescence test. The bismuth mirror as obtained in the usual Marsh's apparatus very closely resembles the antimony mirror, and consists of a strong brown ring in front of the heated spot and a fainter ring behind it. Only about 5×10^{-5} of the bismuth used is converted into the hydride but the optimum conditions have not yet been determined. The luminescence test gives a very satisfactory method of detection of the bismuth hydride. The gases issuing from the Marsh's apparatus are ignited, and a piece of pure calcium carbonate is held on a platinum loop in the flame. The hydride is decomposed and a portion of the bismuth is deposited on the lime. The lime is allowed to cool and is then placed at the edge of the hydrogen flame, when the presence of bismuth is shown by a cornflower-blue phosphorescence. A sky-blue phosphorescence is shown by antimony.

Bismuth hydride is absorbed to some extent by water and 4*N*-sulphuric acid. The gas is absorbed more readily by 0.5*N*-sodium carbonate and *N*-potassium hydroxide, and also by calcium chloride or soda-lime. It is completely decomposed by concentrated sulphuric acid.

Group VI.

The boiling point of sulphur as a standard temperature has been discussed together with the conditions which must be observed.⁵⁸ The vapour pressure over the range 700–800 mm. has been measured and within these limits the relation between temperature and pressure is given by:

$$t = 444.60 + 0.0910(p - 760) - 0.000049(p - 760)^2.$$

By the action of liquid sulphur dioxide on the iodides of sodium, rubidium, and caesium, sulphones of the type $MI_3 \cdot 3SO_2$ have been prepared.⁵⁹ The sodium compound is amorphous, but the other two can be crystallised from their solution in liquid sulphur dioxide. The dissociation pressures of these compounds have been measured between -22.5° and 20.9° , and they show increasing stability with rise in atomic weight of the metal.

The molecular weight of sulphur monochloride in solution in bromoform has been found to correspond with the formula S_2Cl_2 . The freezing point of bromoform is depressed by the addition of sulphur and sulphur monochloride less than the sum of the depres-

⁵⁸ E. F. Mueller and H. A. Burgess, *J. Amer. Chem. Soc.*, 1919, **41**, 745; *A.*, ii, 446.

⁵⁹ R. de Forcrand and F. Taboury, *Compt. rend.*, 1919, **168**, 1253; **169**, 162; *A.*, ii, 341, 366.

sions of these two taken separately. This points to the existence of polythionic chlorides and the highest of these detected in bromoform solution is S_4Cl_2 . It is probable that chlorides richer in sulphur are formed when sulphur is dissolved in the monochloride. It is suggested that the existence of these polythionic chlorides affords an explanation of the formation of polythio-derivatives when organic substances are treated with sulphur monochloride.⁶⁰

In the Annual Report for 1913 the preparation was described of the fluorosulphonates and of sulphuryl fluoride. The ammonium salt, NH_4SO_3F , is most conveniently prepared by the gradual addition of dry ammonium fluoride to sulphuric acid containing about 70 per cent. of sulphur trioxide, and treatment of the product with a small excess of ammonia dissolved in methyl alcohol.⁶¹ The salt melts at 245° and readily reacts with ammonia, especially at low temperatures, to form liquid amines. The alkali metal salts are prepared by the action of the alkali hydroxide on the ammonium salt in aqueous solution. The following have been obtained: KSO_3F , $RbSO_3F$, $LiSO_3F$, and $LiSO_3F \cdot 3H_2O$. These salts can be crystallised from water if the operation is rapidly performed. The alkali fluorosulphonates are very stable towards heat, thus the potassium salt, when heated for some time to bright redness, suffers only slight decomposition, with the evolution of sulphur dioxide, sulphur trioxide, hydrogen fluoride, and oxygen. The barium salt has not been obtained in the pure condition and the crude salt is decomposed at a red heat into barium sulphate and sulphuryl fluoride. This affords the most convenient method for the preparation of sulphuryl fluoride.

The alkali fluorosulphonates possess the remarkable property of exchanging the fluorine atom for an amino-group when treated with an aqueous solution of ammonia or substituted amine.⁶² A portion of the fluorosulphonic acid depending on the strength of the base is hydrolysed to hydrogen fluoride and sulphuric acid, which may readily be removed by chalk or barium hydroxide. In addition to many substituted aminosulphonates the following have been prepared: aminosulphonic acid, barium hydrazinosulphonate, and potassium hydrazinosulphonate. This method of preparation has the great advantage of not requiring the isolation of the base in the anhydrous condition.

An important paper has appeared on the preparation and purifi-

⁶⁰ G. Bruni and M. Amadori, *Atti R. Accad. Lincei*, 1919, [v], **28**, i, 217; *A.*, ii, 281.

⁶¹ W. Traube, J. Hoerenz, and F. Wunderlich, *Ber.*, 1919, **52**, [B], 1272; *A.*, ii, 364.

⁶² W. Traube and E. Brehmer, *ibid.*, 1284; *A.*, i, 434.

cation of selenious and selenic acids, and certain new selenium compounds are described.⁶³ Two sources of selenium were employed, namely, smelter flue-dust and anode slimes from a copper refining works. The flue-dust contained about 22 per cent. of selenium, small amounts of silica, iron, and aluminium, and a trace of tellurium. The flue-dust was finely ground and fused with sodium carbonate and sodium peroxide. The product was treated with water and the insoluble material was filtered off. The filtrate was then nearly neutralised with concentrated hydrochloric acid which precipitated the greater part of the aluminium and zinc as hydroxides. The solution was filtered and the liquid diluted with three times its volume of concentrated hydrochloric acid and boiled for 30 minutes to reduce the selenic acid to selenious acid. Any silica precipitated at this stage was removed by filtration. The filtrate was heated to 80° and treated with sodium sulphite and digested at 80° for several hours to convert the selenium into the grey modification.

The anode slimes contained 96 per cent. of selenium and a considerable amount of tellurium. The dry, finely powdered slime was added to concentrated nitric acid diluted with one-fifth its volume of water. After the vigorous reaction had moderated the mixture was heated to complete the oxidation. The filtrate was evaporated to dryness, the residue dissolved in hydrochloric acid (3:1) and the selenium precipitated by sulphur dioxide or sodium sulphite.

Pure selenium dioxide was obtained by oxidation of the selenium obtained as above with nitric acid and evaporation of the solution to dryness. The selenium dioxide thus obtained was sublimed in a glass tube, the vapours passing through a 2 cm. plug of glass wool.

Pure selenious acid was prepared by the evaporation of the solution obtained by oxidation of the anode slimes by nitric acid until it had a syrupy consistency. The solution on being allowed to remain deposited crystals of selenious acid, and these after four recrystallisations from water were found to be quite free from tellurium.

For the preparation of pure selenic acid three separate methods were employed. In the first silver selenite was oxidised by bromine according to the reaction $\text{Ag}_2\text{SeO}_3 + 2\text{Br} + \text{H}_2\text{O} = \text{H}_2\text{SeO}_4 + 2\text{AgBr}$. The silver salt was suspended in the necessary volume of water to yield a 3 per cent. solution of selenic acid, and bromine water was added until the solution assumed an orange colour. After two hours the precipitated silver bromide was removed by filtration and

⁶³ L. M. Dennis and J. P. Koller, *J. Amer. Chem. Soc.*, 1919, **41**, 949; *A.*, ii, 336.

the excess of bromine removed by a current of air. Silver nitrate solution was then added to precipitate the hydrobromic acid and the solution again filtered. The filtrate was then evaporated on a steam-bath to half its volume and then further concentrated under a pressure of 25 mm. at 120° to remove nitric acid. This process was rendered necessary because it was noted that bromine water when exposed to light gives considerable quantities of hydrobromic acid.

The second method was the oxidation of selenious acid by chlorine in presence of copper carbonate, which dissolves to form cupric chloride and cupric selenate. After the reaction was complete the solution was filtered and evaporated to a small volume at 65° . On cooling cupric selenate separated out and after recrystallisation from water the salt contained only 1—2 per cent. of cupric chloride. The crystals were dried in the air and extracted with acetone in a Soxhlet apparatus to remove the cupric chloride. After one further recrystallisation from water the cupric selenate was found to be pure. Selenic acid was obtained by cautious electrolytic deposition of the copper.

In the third method the selenious acid was converted to selenic acid by anodic oxidation.

It was proved that the electrolysis of selenic acid and its salts under the same conditions as are favourable for the formation of persulphates does not yield either perselenic acid or perselenates. Methods are described for the detection of small amounts of selenious acid in selenic acid, as well as small amounts of sulphuric acid in selenic acid. Very delicate tests are given for the detection of tellurium in the presence of selenium. A method is also described for the estimation of selenium in selenates by the use of hydrazine hydrate.

Copper selenate crystallises from its aqueous solutions with five molecules of water of crystallisation. This pentahydrate on heating at 104° loses $4\text{H}_2\text{O}$ and yields the monohydrate. Complete dehydration is effected at $230\text{--}235^{\circ}$, and the resulting anhydrous salt is stable up to 280° . When the pentahydrate is treated with acetone it is converted into the trihydrate.

Certain ammonia derivatives of copper selenate are described, namely, $\text{CuSeO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$, $\text{CuSeO}_4 \cdot 3\text{NH}_3 \cdot \text{H}_2\text{O}$, and $\text{CuSeO}_4 \cdot 4\text{NH}_3$.

A critical examination has been made of the precipitation of tellurium as the sulphide.⁶⁴ When an aqueous solution of tellurous acid is treated with hydrogen sulphide the tellurium is precipitated as TeS_2 , but from this substance after drying the greater part of the sulphur can be extracted by carbon disulphide. The fact that

⁶⁴ A. M. Hageman, *J. Amer. Chem. Soc.*, 1919, **41**, 329; *A.*, ii, 190.

about one per cent. of sulphur is retained has supported the contention that ordinary tellurium is not a pure chemical element, the suggestion being made that the retention of the sulphur is due to the presence of a more basic element forming a more stable sulphide. There is no doubt that TeS_2 is initially precipitated, but that it is an unstable substance at the ordinary temperature, dissociating into tellurium and sulphur. Below -20° TeS_2 is stable and the velocity of dissociation above that temperature increases as the temperature is raised.

The previous observations as to the impossibility of extraction of the total quantity of sulphur from the compound have been confirmed. After extraction with carbon disulphide for nine days, followed by treatment with boiling alcohol for 30 days, the tellurium still retains at least 0.95 per cent. of sulphur. This residual sulphur does not exist as a sulphide that can be decomposed by hydrochloric or hydrobromic acid, or as an allotropic modification of sulphur insoluble in carbon disulphide. The question as to the condition in which it exists still remains unanswered.

It is shown that the monosulphide, TeS , which has often been described, has no existence.

Group VII.

For the preparation of fluorine the electrolysis of molten potassium hydrogen fluoride or sodium hydrogen fluoride is recommended.⁶⁵ The electrolysis is carried out in an electrically heated copper vessel which serves as the cathode. The anode is made of graphite and is enclosed in a permeable diaphragm, which prevents the hydrogen from mixing with the fluorine. The most efficient conditions are obtained with a current of 10 amperes at 15 volts and a temperature of $240-250^\circ$, when the current efficiency is about 70 per cent. As the electrolysis proceeds, the alkali fluoride and copper fluoride are deposited, and after a time it becomes necessary to regenerate the electrolyte. It is of course necessary that the alkali hydrogen fluoride be absolutely dry, and this is more easily realised with the sodium salt since the potassium salt is hygroscopic. The sodium salt has also the advantage in being less expensive. Moreover, it contains a relatively larger proportion of available hydrogen fluoride and it decomposes below its melting point.

The original investigations^{66, 67} of crystallised sodium hypo-

⁶⁵ W. L. Argo, F. C. Mathers, P. Humiston, and C. O. Anderson, *J. Physical Chem.*, 1919, **23**, 348; *A.*, ii, 332.

⁶⁶ M. Muspratt and E. Shrapnel-Smith, *J. Soc. Chem. Ind.*, 1898, **17**, 1096, 1899; **18**, 210; *A.*, 1899, ii, 281, 533. ⁶⁷ M. Muspratt, *ibid.*, 1903, **22**, 591.

chlorite have been repeated.⁶⁸ The salt was originally found to have a composition corresponding approximately with a hexahydrate $\text{NaOCl}, 6\text{H}_2\text{O}$. In the present investigation the hypochlorite solutions were prepared by treating 35 per cent. sodium hydroxide solution, cooled in ice-water, with chlorine, removing the precipitated sodium chloride, adding sodium hydroxide equivalent to the sodium chloride precipitated, and repeating the treatment with chlorine until the solution was about 5*N*. The solution, which has been freed from precipitated sodium chloride, is cooled to -10° and induced to crystallise by shaking. The sodium hypochlorite separates as a mass of very fine, hair-like crystals filling the whole liquid, whilst the temperature rises considerably. When the whole has again been cooled to -10° the crystals are removed by suction. Considerable difficulty was met with in the analysis of these crystals owing to the fact that they are very deliquescent and also to the fact that they melt between 18° and 19° . The analyses seemed to show that the salt approximates more nearly in composition to a heptahydrate than to a hexahydrate, but further investigation may show that more than one hydrate is present.

The heptahydrate melts to a cloudy liquid and if this liquid is cooled to ordinary temperature large and well-formed crystals of a new hydrate, $\text{NaOCl}, 5\text{H}_2\text{O}$, are obtained. This pentahydrate, melting at 27° , is also very deliquescent, but may be kept unaltered in a well-stoppered bottle.

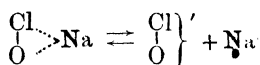
Aqueous solutions of hypochlorous acid containing 25 per cent. of the acid are readily obtained by distilling a mixture of chlorine hydrate and yellow mercuric oxide in a good vacuum.⁶⁹ In attempting to prepare a more concentrated solution or the anhydrous acid by distillation of this solution and condensation of the distillate in receivers maintained at 0° , -20° , and -80° , it was found that in the first two flasks 25 per cent. hypochlorous acid was collected, whilst in the third pure chlorine monoxide condensed. It is evident, therefore, that in the aqueous solution there exists the equilibrium, $2\text{HClO} \rightleftharpoons \text{H}_2\text{O} + \text{Cl}_2\text{O}$. This equilibrium has been investigated by agitating aqueous solutions of hypochlorous acid with carbon tetrachloride at 0° . The equilibrium lies greatly in favour of the hypochlorous acid, for an approximately *N*/5-solution contains 0.2 per cent. of chlorine monoxide. It is probable that the greater oxidising properties of hypochlorites in acid solution are due to the presence of chlorine monoxide.

The absorption spectra of hypochlorous acid, its ethyl ester and

⁶⁸ M. P. Applebey, *T.*, 1919, 115, 1106.

⁶⁹ S. Goldschmidt, *Ber.*, 1919, 52, [B], 753; *A.*, ii, 227.

metallic salts have been observed.⁷⁰ Whilst the acid and ester have the same absorptive power, the salts differ very materially and show well marked absorption bands. This is interpreted to mean that the constitution of the salts and the free acid is different. The authors put forward the view that the acid has the constitution $\text{Cl}-\text{O}-\text{H}$ and that the sodium salt is to be represented by the equilibrium:



Similar differences are found in the case of the chlorites which give the authors another opportunity of making the same suggestion, namely, that the free acid has the constitution $\text{O}=\text{Cl}-\text{OH}$ and the salts the constitution $\text{Cl} \begin{array}{c} \diagup \quad \diagdown \\ \text{O} \end{array} \text{M}$. It is hardly necessary to mention that there is not the slightest evidence in favour of this fanciful suggestion, and that the great mass of experimental evidence is against any such explanation. These substances form typical examples of the same nucleus, $\text{ClO}-$ or ClO_2- , having different energy contents when in combination with hydrogen or an alkyl group and with a metal. Another example is afforded by the nitrates.

A convenient method has been described for the preparation of hydrobromic acid solutions in the laboratory.⁷¹ To 25 c.c. of potassium bromide (containing 15 grams of the salt) are added 0.2 gram of stannous chloride and 3.4 c.c. of concentrated sulphuric acid. By distillation at $120-127^\circ$ a solution of hydrobromic acid is obtained, free from tin and almost free from hydrochloric acid, the yield being 95 per cent.

The red compound, $\text{CaOBr}_2 \cdot \text{H}_2\text{O}$, formed by acting on quicklime with bromine and water in the proportion of 100 grams of lime, 41 c.c. of bromine and 36 c.c. of water, on heating at 100° loses bromine and water, and yields a new basic hypobromite, $\text{CaO} \cdot \text{CaOBr}_2 \cdot \text{H}_2\text{O}$.⁷² This compound is a pale yellow powder and contains about 33 per cent. of available bromine.

Group VIII.

The solubility of the ammonium salts of chloroplatinic, bromoplatinic, and chloroiridic acids in water has been determined at a

⁷⁰ K. Schaefer and W. Köhler, *Zeitsch. physikal. Chem.*, 1919, **93**, 312; *A.*, ii, 207.

⁷¹ A. Pickles, *Chem. News*, 1919, **119**, 89; *A.*, ii, 411.

⁷² J. S. Arthur and L. G. Killby, *Brit. Pat.* 131750; *A.*, ii, 465.

number of temperatures.⁷³ The platinibromide is somewhat more readily soluble than the platinichloride, whilst the solubility of the iridichloride is nearly twice as great as that of the platinichloride. In the presence of ammonium chloride the solubility of ammonium platinichloride and iridichloride is much reduced, but that of the iridichloride is several times as large as that of the platinichloride. Similarly, ammonium bromide reduces the solubility of ammonium platinibromide. In all three cases the reduction in solubility is proportional to the concentration of the ammonium haloid. The difference in the solubility of ammonium platinichloride and iridichloride furnishes a good method for the complete separation of platinum and iridium.

The inhibiting influence of various substances on the absorptive power of palladium for hydrogen has long been known, but only in a qualitative sense. The influence of hydrogen sulphide has now been quantitatively determined and the observations have led to a most interesting and important result.⁷⁴ In the first place it was necessary to fix the conditions of experiment. Since the bulk of the absorbed hydrogen is evolved at 100° in a vacuum, and since also it was advisable to avoid the danger of changing the activity of palladium by heating, it was decided to fix 100° as the maximum temperature at which the metal should be heated.

In the second place it was necessary to determine the amount of hydrogen evolved by a given quantity of palladium at 100°, and also the amount absorbed by this dehydrogenated palladium at ordinary temperature. This volume of hydrogen was found to be 68.5 c.c. for one gram of palladium. On treating the dehydrogenated palladium with hydrogen sulphide it was found that in a few minutes the gas was rapidly absorbed up to about 13.5 c.c. per gram of palladium. This was followed by a slow and continuous absorption of a secondary nature, the total volume of hydrogen sulphide absorbed in 40 hours being 22.5 c.c. per gram of palladium. The hydrogen sulphide thus absorbed was not removed to any great extent by exhaustion at ordinary temperature, this being especially the case when the hydrogen sulphide content of the palladium was comparatively low, and on treatment of the palladium with hydrogen occlusion no longer took place.

On heating the palladium containing hydrogen sulphide in a vacuum at 100° a volume of gas, approximately equal to that of the hydrogen sulphide contained in the palladium, was evolved. This gas, however, was found to consist almost entirely of hydrogen,

⁷³ E. H. Archibald and J. W. Kern, *Trans. Roy. Soc. Canada*, 1917-1918, [iii], 11, 7; A., ii, 70.

⁷⁴ E. B. Maxted, *T.*, 1919, 115, 1050.

the sulphur being retained by the palladium. An interesting observation was made with respect to the specific influence of the sulphur absorption compound on the occlusive power of the palladium for hydrogen, in that, whilst about 13.3 c.c. of hydrogen sulphide are sufficient completely to inhibit the occlusive power for hydrogen of one gram of palladium, the equivalent quantity of sulphur, which remains behind after exhaustion at 100°, is by no means sufficient completely to prevent the occlusion of hydrogen. The influence of the sulphur retained by the palladium after exhaustion at 100° on the occlusive power for hydrogen was quantitatively determined. The mean occlusive power is approximately a linear function of the sulphur content, and each atom of sulphur renders almost exactly four palladium atoms incapable of occluding hydrogen, the remainder of the palladium being capable of occluding normally. This obviously raises the question of the formation of a definite sulphide of palladium, but, as the author points out, there is insufficient evidence to justify such an assumption, and he mentions the fact that palladium foil remains untarnished in pure hydrogen sulphide both at the ordinary temperature and at 100°.

There is no doubt that this result is one of great importance for it may be discussed from an aspect not mentioned by the author, namely, the catalytic activity of the hydrogen occluded by metals. There is little doubt that this activity is due to the supply by the metal of energy to the hydrogen molecules sufficient to dissociate them into atoms. No quantitative data are to hand as regards the number of molecules of hydrogen activated by a given number of metallic molecules. The results described above would seem to afford the first instance of a definite quantitative relation, since four palladium atoms can supply sufficient energy to dissociate one molecule of hydrogen sulphide into a molecule of hydrogen and an atom of sulphur. It is obvious, therefore, how it comes about that more palladium is poisoned by a given volume of hydrogen sulphide than is accounted for by the formation of the Pd_4S complex. In forming this complex one gram of palladium requires about 52.5 c.c. of hydrogen sulphide, and during the formation of this complex 52.5 c.c. of hydrogen are set free. This volume of hydrogen will be absorbed by a further quantity of palladium which will then no longer have any power of absorbing hydrogen. It is not possible from the evidence at hand to calculate the equilibrium conditions which exist.

If, however, Maxted's figure for the poisoning of palladium by hydrogen sulphide is correct, namely, that one gram of palladium is completely poisoned by 13.5 c.c. of hydrogen sulphide, the rela-

tive amounts of energy required to dissociate the molecule of hydrogen into atoms and the molecule of hydrogen sulphide into hydrogen and sulphur may be roughly approximated: 13.5 c.c. of hydrogen sulphide in forming the complex Pd_4S account for 0.257 gram of palladium, and therefore, 0.743 gram of palladium is required to activate 13.5 c.c. of hydrogen. Thus about 12 gram-atoms of palladium are required completely to activate one gram-molecule of hydrogen. Assuming that in each case the amount of energy available from each atom of palladium is the same, it follows that three times as much energy is required to dissociate one molecule of hydrogen into atoms as is required to dissociate one molecule of hydrogen sulphide into a molecule of hydrogen and an atom of sulphur. On the energy quantum theory this would lead to the conclusion that the frequency of the ultra-violet absorption band of hydrogen must be about three times that of the absorption band of hydrogen sulphide.

E. C. C. BALY.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

To have been responsible for a section of the Annual Report for a period of seven years, during the greater part of which the normal course of research was interrupted by the war, has involved on occasions the exercise of a capacity to make the most of limited material, but the facility thus acquired has not enabled the writer to disguise the fact that, in the past year, very little progress has been made in the aliphatic series. The difficulties recently encountered in dealing with publications describing unfinished or disjointed work have been more acute than ever, and, if the experience of one research laboratory is an index of the combined experience of laboratories in general, it is easy to account for the stationary position of this branch of the subject.

Researches which were in progress in 1914 have been completed and published in the interval, or, rather, have in many cases been published without being completed, and there has been but little opportunity to finish any new investigations commenced during the past twelve months. No doubt this state of affairs is transitory, yet it is safe to predict that the future topics of research dealt with in this section will differ widely from those which have been discussed in the past. Chemists have altered their perspective in the course of five critical years, and many may find it difficult to revive an interest in compounds and reactions which are harmless or have no market value. If such be the case, and if utilitarian research is in any sense to overshadow scholarly study, the prospect is deplorable, and the aliphatic series will be one of the first to suffer.

This tendency of the times is already apparent in several branches of the subject where there is little of scientific interest to record. Other factors have, of course, been operative. Political unrest has terminated most of the valuable work on aliphatic hydrocarbons, and must also bear the responsibility for many other gaps in the Report. In addition, the death of Emil Fischer will

profoundly affect further progress in more than one branch of organic chemistry, and a heavy task thus devolves on those who still have the opportunity and still retain the desire to unravel the mysteries of carbon compounds.

It is hoped that the pages of future Reports will show that this responsibility has been realised and successfully undertaken.

Hydrocarbons.

There appears to be every prospect that, for some time to come, most of the investigations on aliphatic hydrocarbons will fall within the province of the Reports on Applied Chemistry. The number of the publications dealing with these compounds certainly remains very much as before, but, for evident reasons, the topics examined have become more and more technical in their nature, and consequently, on the present occasion, discussion may be limited to a comparatively small number of papers.

The somewhat confusing literature on caoutchouc problems, with its contradictory results and periodical corrections, has practically vanished from the pages of the journals. In addition, the researches on the complex unsaturated hydrocarbons, which formerly appeared regularly from Russian sources, have been completely suspended, and these facts are in themselves sufficient to restrict the present section of the Report both in scope and variety. On the other hand, two distinct types of research on hydrocarbons can be readily recognised as engaging most attention. One is the utilisation of natural hydrocarbon gases as sources of aliphatic compounds, and the other, it need scarcely be said, is concerned with the reactions of acetylene. Although in each type potential technical application has been the directing factor, yet the results obtained are frequently valuable from the purely theoretical point of view.

. Considering the somewhat wide range of the problems dealt with in these investigations, it is practically impossible to preserve a systematic arrangement of the subject-matter, but as the "cracking" of natural paraffins has been the object of a considerable amount of research, this problem may be dealt with in the first place. A number of simple saturated hydrocarbons have been selected as test substances, and a general scheme has been put forward in which the conversion of such compounds into aromatic hydrocarbons is claimed to proceed through the consecutive formation of simple olefines, and, in turn, of higher olefines with conjugated bonds. It is not unimportant to note that, in the particular cases studied, the presence of metals does not favour the

production of cyclic hydrocarbons, and they may even act as negative catalysts promoting degradation.¹ Attention has also been paid to the conditions under which tars are formed in the course of these reactions, and it is possible that research of this description may in time throw light on the nature of the complex tars formed by the pyrogenic decomposition of lignified celluloses. This would, of course, involve systematic research conducted on very unpromising materials, but, at the present time, there appears to be a distinct tendency to focus on the problems of polymerisation, and it is well that such is the case. More than passing reference may thus be made to a paper² in which the production of nitroethylene from β -nitroethyl alcohol is described, as the product is not only very easily polymerised, but it has been possible to discriminate between reagents which promote the change and those which retard or even inhibit it. Water proved to be highly effective, but much inferior to alkalis, whilst, on the other hand, acids were found to be without action. In this particular example, the polymerisation is not reversible, and the same holds true in the case of acetylene when the change is promoted by the action of the silent electric discharge. In this connexion, details are now available³ as to the experimental methods by means of which acetylene can be subjected to graded polymerisation by varying the temperature at which the gas is exposed to the discharge, and a striking feature of the products obtained is their ready oxidation and high degree of unsaturation. Whatever the nature of these polymerides may be, they are evidently far removed in structure from benzenoid hydrocarbons, and it would appear that the conversion of acetylene into benzene is by no means so simple a reaction as is generally believed to be the case. The idea has even been put forward that, in pyrogenic reactions at all events, the formation of benzene from acetylene is a secondary change and is preceded by profound decomposition involving the separation of carbon. This is opposed to much experience, but the experiments on which the claim is made were carefully selected and were apparently carried out under highly accurate conditions.⁴ It is always surprising that pyrogenic reactions of acetylene give definite results, considering the somewhat rough and ready manner which characterises much of the experimental work of this nature. Nevertheless, the list of compounds formed in this way continues to grow, and has now been increased by the recognition of *o*-xylene,

¹ J. G. Davidson, *J. Ind. Eng. Chem.*, 1918, 10, 901; *A.*, i, 10.

² H. Wieland and E. Sakellarios, *Ber.*, 1919, 52, [B], 898; *A.*, i, 307.

³ H. P. Kaufmann, *Annalen*, 1918, 417, 34; *A.*, i, 117.

⁴ S. Hilpert, *Ges. Abhand. Kennt. Kohle*, 1917, 1, 271; *A.*, i, 380.

indene, and mesitylene as authentic products. Even the pyrogenic condensation of acetylene and hydrogen sulphide, to which reference has been made in previous Reports, has yielded fresh results in that α -thiotolene and thionaphthen have been detected as additional products of the complex reactions.⁵

Research which is more attractive to the structural and synthetic chemist, and will doubtless yield valuable results in the future, is concerned with the nature of the compounds formed when acetylene combines with mercuric chloride. There is no necessity to discuss the importance of a subject which is evidently the key to the varied reactions of the hydrocarbon under the influence of catalysts, and it now seems reasonably certain that the white compound obtained as the principal product when acetylene acts on mercuric chloride in an aqueous system is, in reality, trichloromercuriacetaldehyde, $(\text{ClHg})_3\text{C}\cdot\text{CHO}$. This view is not without its critics, and it has recently been suggested,⁶ on the basis of a somewhat remote analogy, that the substance is an additive compound of vinyl alcohol. In any case, it is evident that water must have played a part in its formation, and that it arises from a simpler intermediate compound. Twenty years ago it was observed that a second additive compound possessing the composition $\text{C}_2\text{H}_2\cdot\text{HgCl}_2$ is formed in small amount during the reaction, and it is now shown that, by using an alcoholic solution of the metallic chloride, it is possible to obtain the above compound comparatively rapidly and in good yield. Not only so, but the substance is well defined and crystalline, and, considering the yields obtained and the experimental conditions employed, there can be no question but that it represents the first and simplest additive product. Good reasons exist for allocating to it the structural formula $\text{ClHg}\cdot\text{HC}\cdot\text{CHCl}$, and in view of its convenient solubilities and potential reactivity, it may be described as a synthetic reagent with a future.⁷

Although the reactions of acetylene have now become well standardised, novel types are occasionally forthcoming, and an example is furnished by the observation that tetranitromethane can be prepared by absorbing acetylene in concentrated nitric acid in the presence of a mercury salt. Quite apart from the value of the process as a method of preparation, it would appear that the first action of the acid is to form an unstable compound, which is transformed into the nitro-paraffin when heated with acid.⁸ One of the most gratifying signs in recent organic research is the desire

⁵ R. Meyer and W. Meyer, *Ber.*, 1918, 51, 1571; *A.*, i, 72.

⁶ W. Manchot, *Annalen*, 1918, 417, 93; *A.*, i, 145.

⁷ D. L. Chapman and W. J. Jenkins, *T.*, 1919, 115, 847.

⁸ K. J. P. Orton, *Brit. Pat.* 125000; *A.*, i, 247.

to detect, and if possible identify, every intermediate compound formed in reactions, and this policy must make for progress in the end.

Alcohols and their Derivatives.

It seems advisable to discuss all types of alcohols under one heading, as the number of papers dealing with this branch of the subject is much smaller than usual. So far as simple monohydric alcohols are concerned, there is little to report, but it may be mentioned that it is now possible to identify β -aminoethyl alcohol with certainty through the agency of a number of derivatives, the properties of which render them suitable as reference substances. Considering the importance which is attached to β -aminoethyl alcohol, work of this description is by no means valueless, although, in the paper referred to,⁹ another objective can be discerned, as it is impossible to disguise the fact that the synthesis of anæsthetics based on the novocaine model was the main goal of the work.

Now that the preparation of butyl alcohol by the fermentation method has been elevated into a manufacturing process, research in the butane series will be much facilitated. Fermentation butyl alcohol is, however, a mixture, but it is possible to isolate the pure normal form by taking advantage of the fact that the sodium salt of butyl salicylate is easily crystallised, and may thereafter be decomposed with water. The purified *n*-butyl salicylate thus liberated is then converted into the alcohol in the usual way.¹⁰ Another paper describing results which may find application in the laboratory is concerned mainly with the preparation of amylene from commercial amyl alcohol by the catalytic action of aluminium oxide. Although practical directions are now provided whereby uniform yields may be obtained, this reaction has already been studied in some detail, and perhaps greater importance should be attached to the description of a method by means of which amylene may be converted into *tert*.-amyl alcohol displaying a high degree of purity.¹¹

A considerable amount of work has likewise been directed towards improving the preparation of allyl alcohol and of unsaturated alcohols generally, but the results thus obtained do not appear to call for detailed reference. Before leaving the subject, however, mention should be made of a paper in which it is suggested that the formulæ at present assigned to a number of important repre-

⁹ S. Fränkel and M. Cornelius, *Ber.*, 1918, **51**, 1654; *A.*, i, 66.

¹⁰ K. J. P. Orton and D. C. Jones, *T.*, 1919, **115**, 1194.

¹¹ R. Adams, O. Kamm, and C. S. Marvel, *J. Amer. Chem. Soc.*, 1918, **40**, 1950; *A.*, i, 61.

sentatives of the doubly unsaturated alcohol series should be completely rearranged. Basing his views on the evidence provided by a number of transformations undergone by α -citral, the author¹² proposes to assign to geraniol the constitution previously allocated to citronellol, and also to apply Tiemann's formula for geraniol to nerol. This does not exhaust the list of modified formulæ, as, if the above changes are accepted, the constitution of linalool must likewise be altered; but the validity of the argument offered in support of these suggestions cannot well be discussed briefly, although it should be mentioned that the relationship between geraniol and dipentene is readily explained in terms of the constitutions now proposed.

The saturated glycols have also been the subject of considerable study both in the laboratory and in the factory, where, with the object of producing materials which may replace glycerol for industrial purposes, much attention has been paid to the preparation of mixed glycols from waste petroleums. The initial stage is, of course, the cracking of the hydrocarbons to give mixtures of olefines, which are then saturated with chlorine and the products hydrolysed to the corresponding glycols. Numerous patents and papers have dealt with this problem, and one may be quoted¹³ in which the claim is made that the nitrates prepared from these mixed glycols display properties which render them in some respects superior to nitroglycerin¹⁴ as the basis of explosives. In quite a different field, a number of individual glycols have been studied with regard to the molecular transpositions which they undergo when dehydrated, and a lengthy series of papers deals with a large number of fresh examples of such changes.¹⁴ Most of the glycols chosen as test substances are highly substituted by phenyl groups, and much ingenuity has been displayed in utilising the Grignard reagent in the preparation of compounds of diverse type. As a general rule, dehydration of these glycols by means of sulphuric acid gives rise to either a ketone or an aldehyde, and although it is difficult to decipher any important generalisation or novelties in the results, appreciative reference should be made to the work in view of the thorough fashion in which each result has been confirmed.

It is only natural that researches on glycerol should reveal the directing influence of the technical importance of the compound, and it is gratifying to note that many investigations conducted in the factories display a very high standard. The technical pre-

¹² A. Verley, *Bull. Soc. chim.*, 1919, [iv], **25**, 68; *A.*, i, 146.

¹³ H. Hibbert, *Met. and Chem. Eng.*, 1918, **19**, 571; *A.*, 1918, i, 521.

¹⁴ A. Orékhoff, *Bull. Soc. chim.*, 1919, [iv], **25**, 108, and succeeding papers; *A.*, i, 205.

paration of the compound, more particularly by fermentation methods, has recently been prominent, and although this subject does not fall within the limits of the present section of the Report, it is interesting to note how, one by one, the methods are being disclosed whereby the Powers were enabled to supplement their supplies of glycerol, during the War. Reference may, however, be made to one factor which is doubtless of more than passing importance—the fact that the fermentation of sugar by means of a specially resistant yeast is greatly affected by the presence of a reducing agent, such as sodium sulphite. In this way, the yield of glycerol is much increased, a result which is in harmony with the view that glyceraldehyde and dihydroxyacetone are the essential intermediate products in ordinary alcoholic fermentation.^{15, 16}

Before leaving the subject of glycerol, attention should be directed to the application of spectroscopic methods to the problem presented by the existence of two crystalline modifications of glyceryl trinitrate.¹⁷ It is now established that both forms give identical spectra in aqueous solution, and this disposes of the possibility of the two varieties representing chemical isomerides. This conclusion has been well supported by the spectrographic examination of the complete series of partly nitrated glycerols, where, of course, two isomerides are possible in each case, and do exist.

Fresh progress has to be reported in the consecutive scheme of investigations on optically active glycerol derivatives carried out by Abderhalden and his co-workers. Undaunted by many difficulties, they have continued their synthetical work with unflagging zeal, and have now succeeded in obtaining the *d*- and *l*-varieties of a glycerophosphoric acid, which has been isolated in the form of lithium salts displaying opposite activities.¹⁸ The method employed was to introduce the phosphoric acid residue by acting on a pyridine solution of *d*- α -bromohydrin by phosphoryl chloride. The product was thereafter treated with water, and then followed a tedious series of operations designed to remove halogens and pyridine and to obtain crystalline glycerophosphates. There can be no doubt as to the success of the scheme, as lithium glycerophosphate was ultimately obtained in *d*- and *l*-forms, the activities of which are in fair agreement, taking into account the tendency shown by such compounds to form an epihydrin phosphate.

The same authors¹⁹ have also undertaken the preparation of

¹⁵ K. Schweizer, *Helv. Chim. Acta*, 1919, **2**, 167; *A.*, i, 239.

¹⁶ W. Connstein and K. Lüdecke, *Ber.*, 1919, **52**, [B], 1385; *A.*, i, 463.

¹⁷ H. Hepworth, *T.*, 1919, **115**, 840.

¹⁸ E. Abderhalden and E. Eichwald, *Ber.*, 1918, **51**, 1308; *A.*, i, 3.

¹⁹ *Ibid.*, 1312; *A.*, i, 2.

active propylene glycol with the object of synthesising active fats showing a specific rotation sufficiently large to enable enzyme hydrolysis to be studied polarimetrically with a fair degree of accuracy. As is frequently the case with compounds of simple molecular magnitude, the experimental difficulties were considerable, and although active propylenediamine was obtained, the compound proved ineffective as a source of the desired active glycol. An outline of the method which proved successful is given below as an index of the many variations which are frequently necessary in synthetical work of this description.

Allylamine $\xrightarrow{\text{HCl}}$ β -chloro-*n*-propylamine $\xrightarrow{\text{tartaric acid}}$ *d*- β -chloro-*n*-propylamine $\xrightarrow[\text{oxide}]{\text{HONO}}$ *d*- β -chloro- α -propanol $\xrightarrow{\text{KOH}}$ *d*-propylene glycol $\xrightarrow{\text{HCl}}$ *d*-propylene glycol.

Unfortunately, the di-esters of the glycol do not appear to display large rotations, but the work may nevertheless prove useful in the future, and already an additional application of active propylene oxide has to be recorded in that the compound has been used as the indirect source of *l*- β -hydroxybutyric acid. A structural scheme has thus been formulated to show the configuration of this acid, and its relationship to *l*-alanine, but, as in all such cases, the validity of the argument is dependent on the unknown factor as to whether or not optical inversions take place during any of the reactions involved.

As, on the present occasion, the number of publications on the chemistry of esters is too small to justify their discussion under a separate heading, it may be well to include at this stage reference to a highly suggestive paper²⁰ in which the hydrogenation of unsaturated fats is presented in a new light. That this important change, when promoted by the catalytic agency of metals, should show a general resemblance to enzyme action was doubtless to be expected, but the close analogy now displayed between hydrogenation and the enzymatic hydrolysis of glucosides is particularly striking. The most significant result revealed by a study of the time-absorption curves is that an unstable complex is formed between the catalysing metal and the unsaturated fat. This at once brings the reaction into line with standard cases of enzyme hydrolysis, where similarly it has been shown that temporary combination of the catalyst is an essential feature.

²⁰ E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc.*, 1919, [A], 96, 137; *A.*, ii, 403.

Aldehydes and Ketones.

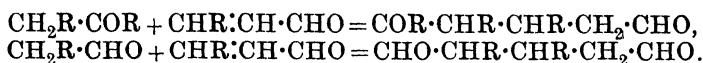
Although numerous papers dealing with the reactions of aldehydes and ketones have appeared during the past year, practically the whole of this work has been conducted on aromatic compounds, and although the results described are not without importance, it is impossible to discuss them in detail in this section. Accepting this restriction, there is but little left to report, with the exception of isolated researches which involve some fundamental points. For example, a return has been made to the problem of classifying ketones according to the relative reactivity of the carbonyl group present, and reference may be made to two papers describing work of this nature. Thus, the condensation of a ketone with ethyl cyanoacetate in the presence of an amino-compound is not a general reaction, and may be either imperfect or completely inhibited, according to the constitution of the ketone chosen.²¹ This represents, of course, merely a rough and ready classification of ketones in terms of one particular reaction, and is incapable of exact treatment. On the other hand, it is possible to classify ketones according to the quantitative reactivity of the carbonyl group through the use of semicarbazide as a test reagent. In the paper now referred to,²² a distinction is properly drawn between reactivity and instability, and the idea is put forward that a carbonyl compound can react with a salt of semicarbazide only after liberation of the free base. If this point be conceded, it follows that the reactive power of any particular ketonic group may be gauged either by using salts of semicarbazide with acids of varying strength or by the addition of excess of an acid to the corresponding salt until a point is reached at which semicarbazone formation is inhibited owing to reverse action. The idea is ingenious, and has been applied to a series of aliphatic ketones, of which propyl isopropyl ketone was found to be the most stable and methyl octyl ketone the most reactive. In this case, also, the classification is based on the behaviour towards one reagent, and the order in which the ketones are arranged in terms of increasing reactivity does not correspond with that deduced from their behaviour with phenylhydrazine, but this does not interfere with due appreciation of a somewhat unique paper and with the prospects opened out of separating closely related ketones by graded reaction.

The only advance which has been noted in synthetical reactions involving aldehydes is a new method for obtaining α -dialdehydes or the corresponding keto-aldehydes. The process depends on the

²¹ I. Guareschi, *Gazzetta*, 1918, **48**, ii, 83; *A.*, i, 94.

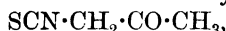
²² A. Michael, *J. Amer. Chem. Soc.*, 1919, **41**, 393; *A.*, i, 253.

alkaline condensation of (a) a ketone or (b) an aldehyde with an ethylenic aldehyde, according to the equations

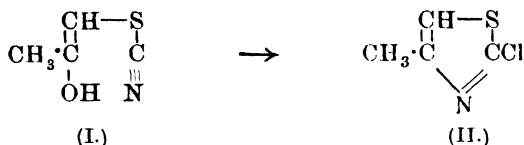


It is true that the examples illustrating the above changes have been selected entirely from the aromatic series, but the experimental details provided seem to indicate that purely aliphatic compounds may also be included within the scope of the general scheme. In any case, the paper in question²³ deserves mention, if only for the light which it throws on many of the tangled results encountered in reactions conducted on the diphenylethane series.

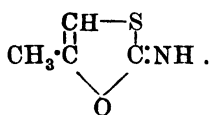
The general problem of the conversion of aliphatic ketones into cyclic structures never seems to lose its attraction, but of several papers on this subject which have been published during the year, discussion may be limited to one.²⁴ Thiocyanacetone



which has now been obtained in a purer condition than hitherto, has been subjected to the action of simple reagents, and, as a result, entirely new ideas are available as to the constitution of compounds previously regarded as thiazole derivatives. Thus, on saturating thiocyanacetone with hydrogen chloride, it is converted into 2-chloro-4-methylthiazole (II), a result which is consistent with the view that the ketone reacts in one of the possible enolic forms



It is, however, conceivable that the tautomeride (I) might undergo rearrangement, involving transference of hydrogen to nitrogen, followed by the closing of the ring through oxygen. Should this occur, the fundamental structure at once diverges from the thiazole constitution, and a series of derivatives should exist related to the type



The name "rhodim" is suggested for this class of substance, and it is now shown that three methylrhodims are readily formed, one

²³ H. Meerwein, *J. pr. Chem.*, 1918, [ii], 97, 225; *A.*, i, 21.

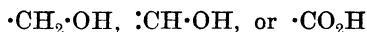
²⁴ J. Tcherniac, *T.*, 1919, 115, 1071.

of which is the compound previously regarded, on very insecure evidence, as hydroxymethylthiazole. This does not exhaust the corrections introduced in a highly interesting paper, as, contrary to Hantzsch's statement, the action of ammonia on thiocyanacetone does not give rise to aminomethylthiazole, although the experiment has been repeated on a generous scale and under conditions favourable to the formation of such a compound.

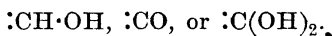
Acids and their Derivatives.

In last year's Report, mention was made of the method of identifying common acids through the agency of their *p*-nitrobenzyl esters, and this useful type of work has now been extended by the application of ω -bromoacetophenone as a reagent. The properties of the phenacyl esters thus obtained are, on the whole, more suitable than those formed from *p*-nitrobenzyl bromide for the characterisation of aliphatic acids. It is now possible to select either of these reagents, the choice being determined by how far the melting point of the expected product is removed from that shown by closely related compounds.²⁵

Before considering more complex subjects, a general paper²⁶ on the oxidation of organic compounds by means of silver oxide may be noted. The subject-matter of the research is naturally as much concerned with alcohols as with acids, but a number of wide generalisations are drawn which reveal the conditions favourable to the formation of carboxy-compounds under mild conditions. Thus, in an alkaline system, silver oxide functions as an oxidiser when any two of the groups



are combined with



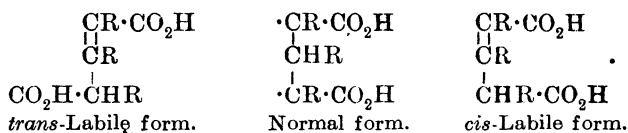
On the other hand, in neutral or acid systems, oxidation proceeds when the secondary alcohol group is united to $\cdot\text{CO}_2\text{H}$, $\text{CH}_3\cdot$, $\cdot\text{CH}_2$, or even H. It is of importance to observe that, in alkaline media, increase in the concentration of alkali affects only the speed of the reaction and not the nature of the products or the proportions in which they are formed. In order to appreciate fully the significance of these results, it is necessary to compare them with those obtained by Nef in his monumental research on the oxidation of carbohydrates by means of Fehling's solution, when it will be seen that both inquiries have led to very much the same conclusions.

²⁵ J. B. Rather and E. E. Reid, *J. Amer. Chem. Soc.*, 1919, **41**, 75; *A.*, i, 157.

²⁶ R. Behrend and K. Dreyer, *Annalen*, 1918, **416**, 203; *A.*, i, 64.

It must be a common experience to find that entirely new ideas present themselves when the constitution of a compound is referred to a structural model different from that usually adopted. A sugar, for example, almost ceases to be a sugar when it is described as a derivative of tetrahydrofuran, but it is occasionally sound policy and a safeguard against impressions becoming stereotyped to regard a carbohydrate in this light. A somewhat similar case, which has the merit of simplicity, has recently been furnished, as it has been pointed out²⁷ that maleic anhydride bears the same relationship to furan as benzoquinone to benzene. The analogy, although imperfect, is fairly well maintained, and extends to the property of the anhydride to give coloured solutions in certain solvents. The effect of saturation or substitution, respectively, to diminish and intensify this property supports the view that a fair parallel exists between the unsaturated anhydride and quinone. The combined results are suggestive, and certainly worthy of attention.

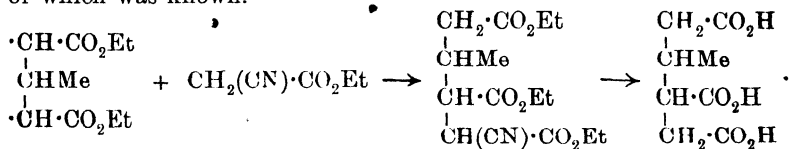
The constitutional problems presented by the glutaconic acids are by no means simple, but, as a result of the systematic researches of Thorpe and his co-workers, it has been possible for some years to provide an adequate explanation of the isomerism displayed by these compounds. Reference to the Annual Reports for 1912 and 1913 will indicate the stage which had been reached when these investigations were interrupted by the War, and it will be recalled that the three isomeric types of a substituted glutaconic acid may be represented by the formulæ



These formulæ are based on numerous reactions, but it is nevertheless difficult to substantiate the structure shown above for the normal type by the production of evidence that addition in the 1:3-positions can take place. Even the reaction with bromine, which proceeds regularly with the labile isomerides, does not take place without molecular rearrangement when applied to a normal form. In the case of the corresponding esters, however, it is possible to discriminate sharply between the normal and labile types, and, at the same time, to confirm the structure assigned to the normal form by taking advantage of the reaction with ethyl sodiocyanoacetate. Hitherto, the opinion has been held that, whereas a labile ester reacts smoothly with this reagent, a normal

²⁷ P. Pfeiffer and T. Böttler, *Ber.*, 1918, 51, 1819; *A.*, i, 62.

form is incapable of reaction except under conditions which promote transformation into a labile isomeride. This view can no longer be maintained, as it is now shown²⁸ that the ethyl ester of β -methylglutaconic acid does actually enter into condensation with ethyl cyanoacetate to give a small yield of the 1:3-additive product. There can be no doubt that the addition did involve the terminal carbon atoms, as the product, when hydrolysed, was converted into γ -methylbutane- $\alpha\beta\delta$ -tricarboxylic acid, the constitution of which was known.



This result, which supplies valuable confirmation of the structural ideas frequently expressed in this series of papers, was not obtained without considerable experimental difficulty.

To turn to another topic, it may be mentioned that some features of general interest are presented in what is presumably the first step in a survey of the properties of aliphatic compounds in which the principal carbon chain is highly substituted by shorter chains. For example, a reaction so well explored as the condensation of a ketone with the ester of an α -iodo-acid does not always proceed in such a manner as to produce a hydroxy-derivative, as it is now found that the corresponding olefinic compound may be formed simultaneously. This has opened up a route to the synthesis of $\alpha\beta\gamma\delta$ -tetramethylhexoic acid, $\text{CH}_3 \cdot [\text{CHMe}]_4 \cdot \text{CO}_2\text{H}$, and the general investigation has incidentally furnished Willstätter²⁹ with a number of new lactones or anhydro-acids which may possibly find application in the varied problems studied by him, even if their importance is not apparent at the present time.

With regard to the metallic salts of aliphatic acids, it is evident that the pyrogenic decomposition of these compounds still continues to be a favourite topic of research, but, of numerous papers describing such work, reference need be made to only one.³⁰ An attempt has been made to classify the metallic formates according to the temperature conditions under which they decompose to give formaldehyde, and also according to their capacity to yield methyl alcohol and acetone, which are the outstanding secondary products of the reaction. The combined results are of importance in connexion with the preparation of aldehydes by the dry distillation

²⁸ J. F. Thorpe, *T.*, 1919, 115, 679.

²⁹ R. Willstätter and D. Hatt, *Annalen*, 1919, 418, 148; *A.*, i, 431.

³⁰ K. A. Hofmann and H. Schibsted, *Ber.*, 1918, 51, 1398; *A.*, i, 7.

method, as it has been shown in the course of the work that zinc formate is the most suitable substance for the production of form-aldehyde.

It is impossible to leave the consideration of metallic salts without reference to a type of investigation which, although more appropriately dealt with in another part of the Report, has been in the past the object of appreciative reference in this section. In recent years, our ideas on the nature of soap solutions have altered profoundly, largely owing to the discovery that such solutions display an unexpectedly large conductivity in concentrations where the result cannot be attributed to hydrolysis. The explanation which has been put forward to account for this behaviour is that an aggregation of charged ions forms the nucleus of the colloidal particle, and that the system thus produced, termed the "ionic micelle," is responsible for a large proportion of the conductivity. The general terms of this theory have frequently been expressed in the course of a lengthy series of investigations on soap solutions, and in the latest contribution³¹ it has been formulated in greater detail and supported by a series of conductivity, freezing-point, and vapour pressure determinations carried out on solutions of pure soaps at ordinary temperatures. A study of the results, and more particularly of the form of the conductivity curves, shows that the theory accounts adequately for the known facts, and, in view of the increasing importance now attached to the electrical condition of colloids, its elaboration is both important and opportune.

Halogen Compounds.

In normal times, difficulty was always encountered by the reviewer in any attempt to discuss researches on halogen derivatives under one general heading, as the synthetic applications of these compounds penetrate into every branch of the subject. The past year has, however, been exceptional, as, in the aliphatic series at least, the use of halogen compounds in syntheses has not only been restricted in scope, but presents no feature of novelty. On the other hand, several papers have dealt with improved methods of preparing simple haloids, and reference may be made to some examples which may reasonably be expected to find application in the laboratory.

The general development under which petroleum gases are now being used as the starting material in the preparation of fatty compounds of varied type has been extended to the formation of

³¹ J. W. McBain, (Miss) M. E. Laing, and A. F. Titley, *T.*, 1919, **115**, 1279.

simple aliphatic haloids. For example,³² a natural gas consisting principally of methane containing a small proportion of ethane, has been found to undergo progressive substitution when, in admixture with chlorine, it is passed through a heated tube containing a suitable catalyst. It is not surprising to find that, in the search for a catalysing medium, anti-gas charcoal was tried and found to be highly effective, but, of necessity, the process gives mixtures of chloro-compounds, although it appears possible to grade the reaction so as to yield either carbon tetrachloride or chloroform as the essential product. So far, this method of chlorination has been conducted with comparatively small quantities of material, but it is probable that it may be developed into large-scale working, and, if so, there are many outlets for the mixture of chlorides which may thus be obtained. It is, however, doubtful if the method can compete with the parallel process in which petroleum is cracked to give olefines, and these are converted in turn into the corresponding dichlorides, as, in each case, the products are mixtures and will probably be used mainly as solvents.

Another method of preparing aliphatic chlorides, the utility of which is equally doubtful in view of the fact that mixtures of isomerides are formed, depends on the direct action of hydrogen chloride on an alcohol, the mixed gases being led over aluminium oxide at a moderate temperature. Scrutiny of the results obtained³³ shows that, under these conditions, the tendency of the alcohol to pass into the corresponding olefine cannot be altogether excluded, and thus the products, except in the simplest cases, are not individual compounds, but contain secondary, and even tertiary forms in addition to the primary chloride. Of greater importance from the point of view of laboratory working is the account of an improved method for preparing alkyl iodides.³⁴ The process is really a modification of that recommended by Walker, as the appropriate alcohol is boiled in contact with a mixture of yellow and red phosphorus, the iodine being introduced by means of the refluxing liquid. The working details supplied in this latest contribution to the scheme for facilitating the laboratory preparation of research reagents will be welcome, as it is a distinct advantage to have a safe and economical method of preparing the simple iodides at the rate of several kilograms a day.

It is evident that, despite prolonged investigation, the complica-

³² G. W. Jones and V. C. Allison, *J. Ind. Eng. Chem.*, 1919, **11**, 639; *A.*, **i**, 429.

³³ P. Sabatier and A. Mailhe, *Compt. rend.*, 1919, **169**, 122; *A.*, **i**, 430.

³⁴ R. Adams and V. Voorhees, *J. Amer. Chem. Soc.*, 1919, **41**, 789; *A.*, **i**, 306.

tions encountered in attempts to prepare chloroform by electrolytic methods are far from being removed. Great possibilities are contained in such a process, but the usual practical difficulties regarding the choice of the most favourable conditions of current density, temperature, and concentration are increased by the fact that the accumulation of alkali at the cathode has the effect of decomposing the liberated chloroform. By the adoption, however, of a neutralisation electrode it is possible³⁵ to minimise this loss, but nevertheless the method is complicated and somewhat uncertain in its results. Even under carefully standardised conditions the yields of chloroform obtained from acetone are throughout inferior to those given by alcohol when the electrolysis is conducted in the presence of the chlorides of alkali or alkaline-earth metals. This is not surprising in view of the fact that when alcohol is employed the first step of the reaction is the formation of acetaldehyde, the conversion of which into chloroform by means of calcium hypochlorite is stated³⁶ to be instantaneous and quantitative.

As already mentioned, no novel synthetical uses of halogen compounds have been noted, but a passing reference may be made to some complicated results which have been obtained by the interaction of magnesium phenyl bromide and halogenated ethanes. The essential feature of these reactions is the fact that when substitution of the paraffin molecule has been effected by different halogen atoms, these are in part eliminated under the action of the reagent. Although little uniformity can be discerned in these results, the investigation will prove useful to those who have occasion to act with Grignard reagents on poly-halogen compounds.³⁷ Greater satisfaction will be found in the study of an investigation³⁸ in which the action of Grignard reagents on the esters of aliphatic dibasic acids has been controlled, so that the change is limited to one carboxy-alkyl group. A considerable amount of attention has in the past been paid to the problem of modifying the Grignard reaction, so as to attack preferentially one of two groups which are apparently symmetrical. In the case of di-esters, complete reaction on normal lines should give a ditertiary glycol or a closely related compound, and practically without exception results of this nature have been obtained when compounds of the type of diethyl oxalate, malonate, or succinate are subjected to the action of Grignard reagents. It is now shown, however, that the limitation of the reaction to one position is largely a matter of restricting the proportion of mag-

³⁵ J. Feyer, *Zeitsch. Elektrochem.*, 1919, **25**, 115; *A.*, i, 305.

³⁶ S. Uthelm, *Brit. Pat.* 113094; *A.*, 1918, i, 521.

³⁷ F. Swarts, *Bull. Soc. chim.*, 1919, [iv], **25**, 145; *A.*, i, 247.

³⁸ H. Hepworth, *T.*, 1919, **115**, 1203.

nesium alkyl haloid employed, although the special method adopted to incorporate the reacting substances may also be a factor. In this way it has been possible to prepare α -hydroxy- α -ethylbutyric acid from ethyl oxalate and magnesium ethyl bromide, and this single example will be sufficient to illustrate the nature of the reaction. This appears to be perfectly general, as the only exception encountered in a number of test cases was that of ethyl malonate, where enolisation interfered with the normal course of the change.

It is always of interest to encounter transformations from the aliphatic to the aromatic series which can be described as syntheses in the best sense of that expression, and another example³⁹ has been added to the existing list in that malonyl chloride reacts with acetone with the elimination of two molecular proportions of hydrogen chloride, and the formation of phloroglucinol as the essential product. The blackboard representation of this reaction will doubtless, on account of its simplicity, find application in the lecture-room, and it is more than probable that an intermediate product formed in the condensation will prove useful in the laboratory, if the constitution assigned to it, namely, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COCl}$, is correct. A compound which has a six-carbon chain, is a diketone, and also an acid chloride is at once stamped as embodying endless possibilities.

Optical Activity.

The idea was expressed in last year's Report that it is inadvisable to limit the review of optical activity entirely to examples selected from the aliphatic series, and on the present occasion effect is given to the suggestion then put forward that all types of optically active compounds should be discussed. It is difficult to present this subject in any order which has the merit of logical continuity, and, in such a case, it may be well to begin by an account of new resolutions which have been effected during the year. Of several examples, most interest will be attached to the revised specific rotation of tropic acid, the two active forms of which have been isolated under conditions which guarantee their optical purity. Curiously enough, this has been achieved in the course of two separate investigations which differed widely so far as the initial topic of research was concerned. With regard to one of these inquiries it must be admitted that the detailed stereochemistry of the alkaloids is beyond the scope of this section of the Report, but it should nevertheless be stated that a distinct advance has been made in characterising two out of the eight possible active

³⁹ T. Komminos, *Compt. rend.*, 1918, 167, 781; A., i, 6.

hyoscines. Starting from the feebly active hydrobromides obtained in the manufacture of *l*-hyoscine, the *d*-form has been isolated through the agency of *d*- α -bromo- π -camphorsulphonic acid. In addition, *l*-hyoscine was hydrolysed, not by alkali, as is usually the case, but by means of acid, and in this way *l*-tropic acid was obtained, displaying an activity somewhat higher than the standard value hitherto accepted. It was thus desirable to repeat the resolution of tropic acid so as to establish the maximum rotatory power, and this was accomplished by the successive use of quinine and quinidine.⁴⁰ By a coincidence the values obtained by King were confirmed in the course of an investigation,⁴¹ in which the standard synthetical methods of preparing π -tropic acid have been tested and found to be in many respects unsatisfactory. Exact working details are now provided, by means of which the compound may be obtained in good yield by the operation of a synthetical scheme in which acetophenonecyanohydrin is the starting material. In resolving the acid, quinine was used to separate the *d*-form, and morphine was found to give the most satisfactory results in the isolation of the optical isomeride. The rotatory powers of this important acid have thus been established with a high degree of accuracy.

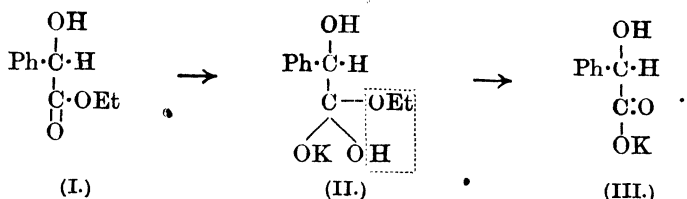
Turning to reactions conducted on optically active compounds, Abderhalden's recent work on derivatives of glycerol has already been dealt with, so that it is possible to pass to the consideration of examples which illustrate in how far the mechanism of reactions may be indicated through a study of optical changes. On first inspection the subject of racemisation does not appear to be a promising source of new ideas regarding the process of ester hydrolysis, but nevertheless the complexity of such changes is well revealed by considering the optical effects encountered in hydrolysing ethyl *l*-mandelate under different conditions.⁴² It may now be regarded as a general rule that alcoholic potassium hydroxide exercises a more powerful racemising effect than aqueous alkali in the hydrolysis of an active ester, and the result cannot be attributed to the action of the alkali on the liberated acid, as this is a minor effect compared with the direct racemisation of the non-hydrolysed ester. It follows that the mechanism of hydrolysis is different according as aqueous or alcoholic alkali is used, and it is reasonable to assume that potassium ethoxide rather than potassium hydroxide is to be regarded as the essential racemising agent. It is now suggested that, in the case of aqueous hydroxide, an additive compound is formed which afterwards loses the elements of alcohol, and thus

⁴⁰ H. King, *T.*, 1919, 115, 476.

⁴¹ A. McKenzie and J. K. Wood, *ibid.*, 828.

⁴² A. McKenzie and H. Wren, *ibid.*, 602; *A.*, i, 326.

gives the potassium salt directly as shown below in the specific example of ethyl *l*-mandelate:

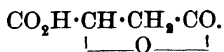


As the groups added and eliminated are not immediately connected with the asymmetric carbon atom, it follows that if (I) is laevorotatory, (III) will be active in the same sense. On the other hand, when alcoholic potassium hydroxide is employed it may be assumed that the above compound (II) is replaced in part by (IV), so that the elements of alcohol can be eliminated only by the formation of



the unsaturated type (V). In the presence of water this would pass into the two active forms of mandelic ester, and as these would be produced in equal amounts total racemisation would result. The theory is in harmony with the facts, and explains the partial racemisation of the non-hydrolysed ethyl *l*-mandelate which remains when the pure active ester is treated with alkali in insufficient amount to cause complete hydrolysis. The combined results and the use which has been made of them constitute a good example of the application of optical methods in tracing the mechanism of reactions generally regarded as simple.

In an entirely different field, optical changes have been used to expand our ideas regarding the reactions of the halogenated succinic acids. In this work, Holmberg has frequently emphasised the idea that the removal of halogen from these compounds involves the transient formation of active malolactone,



The existence of such a lactone has been predicted largely from the results of physical measurements, but the compound has now been isolated in *r*- and *s*-forms. This has been possible through the preparation of pure iodosuccinic acid, the optical behaviour of

which, it may be mentioned, is very similar to that displayed by the corresponding bromo-compound.⁴³ When treated with silver oxide and water *d*-malo-lactone was formed, and the properties of this product agree closely with those ascribed to it before its isolation had been accomplished. Thus, when the lactone ring was opened by means of acid some racemisation took place, but the malic acid produced contained excess of the *l*-form. With alkali no racemisation occurred, but *d*-malic acid was alone produced.⁴⁴ This result must be regarded as highly satisfactory, as is also the fact that the views formerly expressed⁴⁵ as to the reaction between *l*-bromosuccinic acid and potassium xanthate have now been experimentally confirmed.⁴⁶

It is inevitable that papers which involve closely sustained and continuous argument cannot readily be reviewed within the narrow compass of the Reports, and this applies to the latest contribution⁴⁷ to the vexed question of the causes which are responsible for anomalous dispersion. Attention is thus directed to the original paper, which deals with the rotation dispersion of the higher ethereal tartrates, and introduces a number of arguments opposed to the view that abnormal dispersion is to be attributed to the co-existence of dynamic isomerides displaying different rotatory powers. It is equally difficult to do justice to another paper,⁴⁸ which deals with a new quantitative generalisation governing optical activity in the sugar group. The number of acid amides related to the sugars which have been obtained in a pure condition has recently been increased, and, as pointed out last year, the optical activity of such compounds is largely dependent on the configuration of the groups attached to the α -carbon atom. It is now possible, through the analysis of the rotations shown by the acid amides from the C_4 to the C_7 series, to ascribe a quantitative value to the optical effect contributed by the $\alpha\beta\gamma\delta$ -asymmetric systems of a sugar. This may appear to be a bold claim, particularly as the generalisation depends on the exact application of the principle of superposition to sugars, but, at the same time, it is evident that the values now quoted will serve as a valuable guide in determining the constitution of partly substituted aldoses and in indicating which hydroxyl group has been substituted.

⁴³ B. Holmberg, *Arkiv Kem. Min. Geol.*, 1917, 6, No. 23, 33; *A.*, 1918, i, 523.

⁴⁴ B. Holmberg, *Svensk. Kem. Tidskr.*, 1918, 30, 190, 215; *A.*, i, 309.

⁴⁵ *Ann. Report*, 1917, 83.

⁴⁶ B. Holmberg and K. J. Lenander, *Arkiv Kem. Min. Geol.*, 1917, 6, No. 17, 26; *A.*, 1918, i, 529.

⁴⁷ P. F. Frankberg and F. H. Gerner, *T.*, 1919, 115, 636.

⁴⁸ C. S. Hudson and S. Komatsu, *J. Amer. Chem. Soc.*, 1919, 41, 1141; *A.*, i, 524.

The first step in what may prove to be an inquiry of considerable significance in biology is marked by the preparation of *d*- and *l*-forms of simple dyes containing an asymmetric system.⁴⁹ The work has not proceeded far, but evidence has already been obtained that these optical isomerides are selectively absorbed by wool, and the prospect is thus opened out that they may ultimately be used in the staining of sections so as to reveal more completely the chemical constitution of tissues. This field of research has not been explored by the chemist, and there is ample scope for future developments of great importance.

Carbohydrates.

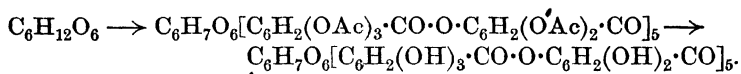
Any advances which may recently have been made in our knowledge of the carbohydrates are largely discounted by the fact, to which reference has already been made, that the great pioneer in sugar synthesis died during the year. This is not the occasion, even if space permitted, to make any attempt to pay fitting tribute to the inspiration and instinctive genius which characterised Emil Fischer's best work on the sugar group, and it is perhaps sufficient to say that, master in more than one branch of organic chemistry, he was, above all, the master of sugar chemistry. He has left behind him a record in carbohydrate research which many may imitate, but none can excel.

In so far as publications reflect the methods of the man, a worthy model is discernible in Fischer's papers which well repay careful study even by those who have no special interest in the sugars. He had an extraordinary capacity to formulate schemes of research which were apparently disconnected, and then finally to marshal the results in order, so that each fitted into its appointed place, making a complete story.

It is appropriate that, on this occasion, a departure should be made from the customary order in which the carbohydrates have been dealt with in recent Annual Reports, and to consider in the first place the publications which mark the close of Fischer's career. It will be recalled that, in 1912, he propounded the view that certain tannins may be regarded as fully esterified glucoses, in which digalloyl residues substitute the hydroxyl groups. Despite many unexpected difficulties and distractions, he continued with characteristic courage to test his ideas by means of syntheses, and from the time he succeeded in devising a method for the preparation of the penta-acetyl-*m*- and *p*-digalloyl chlorides, it was evident that he had secured the reagents which would make success possible. He

⁴⁹ C. W. Porter and C. T. Hirst, *J. Amer. Chem. Soc.*, 1919, **41**, 1264; *A.*, **i**, 558.

lived to see his hopes realised. By acting on glucose with either of the above acid chlorides, the corresponding penta-(penta-acetyl-digalloyl)-glucoses were obtained, and, on further treatment with aqueous sodium hydroxide, the acetyl groups were removed, with the formation of a penta-digalloyl-glucose:



Exclusive of the obvious *m*- and *p*-isomerism which may be contributed by the digalloyl residues, the capacity of the glucose component to exist in diverse modifications has to be taken into account, so that the structure formulated above may be represented by several compounds. Fischer found, however, that penta-(*m*-digalloyl)- β -glucose resembles natural Chinese tannin closely, and the corresponding α -compound likewise shows a general agreement, although displaying a different specific rotation. In work of this description, divergency in specific rotations ought not to weigh heavily in judging the success of a synthesis. Scrutiny of some of Fischer's experimental results, such as the effect of acetylation on both synthetic and natural tannins, reveals the delicacy of these complexes and their ready tendency to undergo intramolecular changes. It would have been in the highest degree surprising if the specific rotations of natural and synthetic tannins had corresponded exactly, particularly as these values are determined on colloidal systems. It may thus be taken that a tannin synthesis has been effected, but considering that our views on the structure of sugars are at present in a state of flux, it must be admitted that the problem of the constitution of tannin is far from having been solved. Perusal of the two papers^{50, 51} describing the results reviewed above indicates sufficiently the difficulties encountered, and the publications deserve careful study in view of the suggestive variations introduced into ordinary working methods. Incidentally, in the course of the work a number of minor points have been cleared up, and the patience with which these side-issues have been examined commands admiration. For example, the existence of a definite glucogallin in Chinese rhubarb has always been regarded as indirect evidence in support of the idea that the glucose formed by the hydrolysis of tannin is not adventitious, but represents a specific cleavage product, yet numerous attempts to synthesise this apparently simple compound have given most conflicting results. There can be no longer any doubt as to the nature of glucogallin, which has been synthesised by the interaction of acetobromoglucose and

⁵⁰ E. Fischer and M. Bergmann, *Ber.*, 1918, **51**, 1760; *A.*, i, 87.

⁵¹ *Ibid.*, 1919, **52**, [B], 829; *A.*, i, 278.

silver triacetyl-gallate, followed by removal of the acetyl groups. This proves that glucogallin is 1-galloyl- β -glucose, and the compound is thus differentiated from β -glucosidogallic acid.⁵²

Fischer's views as to the structure of a typical tannin have been supported indirectly by the observation⁵³ that, in the presence of boric acid the conductivity of tannin isolated from the gall-nut is notably increased. Moreover, the exaltation observed is consistent with the idea that, although there are twenty-five hydroxyl groups in the molecule, these are distributed in such a manner that only ten pairs are favourably situated for combination with the acid. This is a striking result, but unfortunately it does not throw any light on the stereochemical condition of the sugar residue, and the same result would be given by a complex consisting of a monosubstituted glucose with the necessary hydroxyl groups in a single side-chain. It is appropriate that Fischer's work on tannin should be continued by those with whom he was associated in his earlier investigations on this subject. Freudenberg's latest contributions to the general problem include an attempt to identify the unknown hexose present in hamameli-tannin,⁵⁴ and the isolation from chebulic acid of a new crystalline tannin which apparently possesses the comparatively simple composition of a digalloylglucose. Before leaving this subject it may be mentioned that, in his closing papers, Fischer adopted the numerical method of indicating the position of substituents in sugar derivatives, and the fact may be used as an argument, where other arguments have failed, in favour of the adoption of this measure of relief to the distracted workers on related topics.

It need scarcely be pointed out that Fischer's synthesis applies to one particular type of tannin only, and that the nature of other classes of tannins still remains obscure. A conspicuous example of this is furnished in the case of hemlock tannin. In the course of an exhaustive experimental study, it has been shown that this complex contains no sugar chain, and the authors of an important paper,⁵⁵ confronted as they were with a mass of difficult experimental results, prudently refrain from expressing any opinion as to the detailed constitution of the compound.

⁵² E. Fischer and M. Bergmann, *Ber.*, 1918, **51**, 1804; *A.*, i, 89.

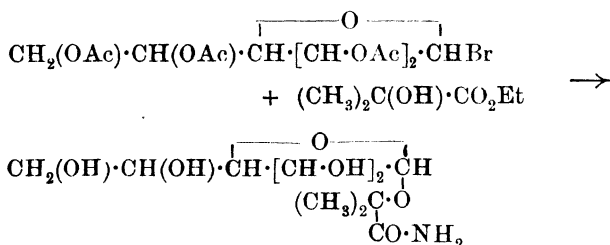
⁵³ J. Böseken and W. M. Deerns, *Proc. K. Akad. Wetensch. Amsterdam* 1919, **21**, 907; *A.*, i, 412.

⁵⁴ K. Freudenberg, *Ber.*, 1919, **52**, [B], 177; *A.*, i, 215.

⁵⁵ R. J. Manning and M. Nierenstein, *T.*, 1919, **115**, 662.

Glucosides.

From the tannins it is but a step to the consideration of the glucosides proper, and here also it is appropriate that Fischer's last work should have been crowned with success. Reference was made in the Annual Report for 1917 (p. 79) to the variation he introduced into glucoside synthesis, whereby nitrile-glucosides may be obtained from hydroxy-esters, and, although the experimental difficulties encountered are probably more severe than is indicated in the published papers, there seems no doubt that the methods are widely applicable and extend to cases where an aliphatic nitrile is coupled with the glucose residue. To take a case in point, acetobromoglucose has been condensed with ethyl α -hydroxyisobutyrate, and, on treating the product with ammonia, the acetyl groups are lost with the ultimate production of hydroxybutyramide glucoside:



Finally, dehydration of the amide gives the nitrile-glucoside, which, in the example given, proved to be linamarin.⁵⁶ Although the scheme given above represents the essential steps, considerable variation in procedure is evidently necessary in order to obtain crystalline products, and when the conversion of the acid amide into the nitrile is effected by means of phosphoryl chloride, the product requires re-acetylation. Obviously, the general reaction may be modified so as to produce a wide variety of synthetic glucosides of the cyanogenetic type, and the interesting cases furnished by the glucoside of glycollonitrile⁵⁷ and the corresponding celloside⁵⁸ give promise that the chemistry of amygdalin may now be attacked synthetically.

It is not a severe criticism to state that the remaining publications on glucosides fall far short of those just reviewed. The heroic efforts of Kiliani to unravel the complications of the digitalis glucosides have not been suspended, although positive results are few in number, and no more than a passing reference need be made to the

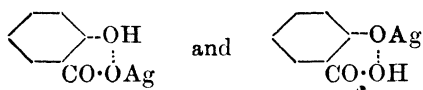
⁵⁶ E. Fischer and G. Anger, *Sitzungsber. K. Akad. Wiss. Berlin*, 1918, 203; *A.*, 1918, i, 526.

⁵⁷ E. Fischer, *Ber.*, 1919, 52, [B], 197; *A.*, i, 256.

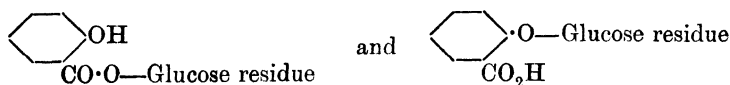
⁵⁸ E. Fischer and G. Anger, *ibid.*, 854; *A.*, i, 256.

latest contributions to the subject.^{59, 60.} In difficult work of this description it is somewhat disappointing to find that complications are needlessly introduced through the occasional choice of a reagent which appears in the highest degree unsuitable, but the devotion of the investigator is most commendable. Other work which, although only remotely concerned with the sugar group, similarly arouses feelings of sympathetic admiration is the first step in yet another attempt to isolate an enzyme in a state of analytical purity. The research referred to opens up a large number of important questions, and as the programme contemplated is ambitious, it is well that it is in competent hands,⁶¹ but, as a side-issue which may yet prove to be important, it may be mentioned that the peroxidase of the horse-radish is associated with a nitrogenous glucoside the properties of which, so far as they are described, point to a close relationship with glucosamine.

Two years ago attention was directed in the Reports to the fact that, when silver salicylate reacts with acetobromoglucose, two isomeric products are formed and the explanation then offered as to the underlying mechanism of the reaction has now been confirmed.⁶² It has long been recognised that when the silver salt method of esterification is applied to α -hydroxy-acids an abnormal result is obtained in that, to some extent, the alkyl group introduced substitutes the hydroxy-position. The same holds true in the case of α -amino-acids, and the most obvious interpretation is that in silver salts of the type mentioned, the metallic atom is attached, not only to the carboxyl, but also to the hydroxy- or amino-position. According to this view, silver salicylate would be represented as



and consequently the glucosides obtained from such a structure by the action of acetobromoglucose would display the isomerism shown below:



It is a curious fact that, as a reagent, acetobromoglucose is specially well adapted for the display of this isomerism, of which several new

⁵⁹ H. Kiliani, *Ber.*, 1918, **51**, 1613; *A.*, i, 90.

⁶⁰ *Ibid.*, 1919, **52**, [B], 200; *A.*, i, 214.

⁶¹ R. Willstätter and A. Stoll, *Annalen*, 1918, **416**, 21; *A.*, 1918, i, 555.

⁶² P. Karrer, C. Nägeli, and H. Weidmann, *Helv. Chim. Acta*, 1919, **2**, 242; *A.*, i, 338.

examples are now described. As an interesting side-issue of the research in question, it may be remarked that the resolution of inactive mandelic acid was achieved by taking advantage of the different solubilities of the glucosides, but evidently, if this method is to receive application, due attention must be paid to the formation, on the lines indicated above, of glucosido-acids.

Monosaccharides and their Derivatives.

To turn to the apparently simple subject of the monosaccharides there is little of outstanding interest to report. As has recently been the case, a number of improved methods of preparation of sugars and related compounds have been described, and amongst these may be mentioned convenient processes for the isolation of rhamnose,⁶³ and of gulonolactone.⁶⁴ There is generally something definite about methods of preparation, but it is difficult to express an opinion on the new sugar *floridose*, which, although claimed to be an unknown aldohexose, displays a suspicious similarity to galactose.⁶⁵ It is just possible that the compound may be a variety of galactose corresponding with one of the abnormal galactose penta-acetates, but an opinion on this point must in the meantime be withheld.

On first inspection, a research on the properties of γ -hydroxy-valeraldehyde may seem to have little connexion with the sugar group, but the compound, which has been obtained in an ingenious manner,⁶⁶ is suitable for testing the idea that aldehydic and hydroxyl groups when separated by a chain of three carbon atoms undergo mutual rearrangement to give a butylene oxide. The aldehyde in question certainly displays most of the reactions of a reducing sugar, and as it gives a "methylglucoside," an additional argument is thus forthcoming in support of the current view of sugar structure. The critic may find some inconsistencies in the evidence, and it is unfortunate that the absence of optical activity places limitations on the search for analogies, but this does not detract from the appreciation of the treatment of an interesting subject. Work of a similar nature might with advantage be conducted on α -, β -, and δ -hydroxy-aldehydes in view of the obscure isomerism of sugars to which attention has been directed in recent years. In addition, the physical examination of sugars requires considerable

⁶³ E. P. Clark, *J. Biol. Chem.*, 1919, **38**, 255; *A.*, i, 387.

⁶⁴ F. B. La Forge, *ibid.*, 1918, **36**, 347; *A.*, i, 65.

⁶⁵ E. Takahashi, *J. Tokyo Chem. Soc.*, 1919, **40**, 157; *A.*, i, 387.

⁶⁶ B. Helferich, *Ber.*, 1919, **52**, [B], 1123; *A.*, i, 386.

expansion, and thus a further study⁶⁷ of the mutarotation of glucose and fructose is welcome, even admitting that this phenomenon has already been thoroughly examined. The fact that temperature affects the rotation equilibrium of the ketose is not new, but it is highly significant that, in this special case, mutarotation cannot be regarded as due simply to a change in the position of one hydroxyl group. This adds to the evidence that fructose exists in solution in more than two forms.

It is with considerable reluctance that no detailed account is given here of Levene's efforts to advance the difficult chemistry of the amino-sugars, but the experimental treatment of the subject is such that results leading to final conclusions as to configuration are, of necessity, delayed until the full scheme of research is complete. It would thus be premature, and also an injustice to a carefully conceived series of researches, to discuss the intermediate results so far contributed, but reference should be made to the papers which have appeared during the year. In order that the investigations may be followed, it should be mentioned that the goal of the work is the allocation, to a definite configuration, of the amino-group present in compounds of the glucosamine type. The method of attack is to study the corresponding amic acids, rather than the sugars to which they are related, and to pay particular attention to the compounds which form epimeric pairs. The difficulty in preparing these hexosamic acids or their epimerides⁶⁸ and the complications involved in the removal of the amino-group by nitrous acid,⁶⁹ can be fully appreciated only by those whose work has led them into this field. In the latest publication on this subject⁷⁰ a distinct advance has been made in that the epimeride of glucosamine has been isolated and described. The reactions of the compound are normal save in two respects. No monocarboxylic acid has yet been obtained from it, and, curiously enough, when treated with nitrous acid, no molecular dehydration took place, but saccharic acid was formed. Nevertheless, the sugar is readily converted into the analogue of chitose, and this was isolated in the crystalline condition. Some confusion of ideas seems to exist as to the reasons underlying the failure of epichitosamine to display mutarotation, and until the free sugar has been obtained in α - and β -modifications in which definite configurations can be allocated to the reducing groups, it is altogether premature to delete from consideration a betaine structure for this and analogous compounds.

⁶⁷ J. M. Nelson and F. M. Beegle, *J. Amer. Chem. Soc.*, 1919, **41**, 559; *A.*, i, 256.

⁶⁸ P. A. Levene, *J. Biol. Chem.*, 1918, **36**, 73; *A.*, 1918, i, 530.

⁶⁹ *Ibid.*, 89; *A.*, 1918, i, 532.

⁷⁰ *Ibid.*, 1919, **39**, 69; *A.*, i, 475.

Disaccharides.

Recently the contributions under this heading have shown a distinct falling away in number, but the quality of the work described has been well maintained. Synthesis by means of enzyme action continues to make progress, and amongst new results may be mentioned the formation of gentiobiose as one of the products obtained in a reaction designed to produce glycol glucosides by the synthetic action of emulsin.⁷¹ In view of the earlier synthesis of gentiobiose the result is not surprising, but the auto-condensation of glucose is not restricted to one type of coupling, cellobiose having been isolated as the fourth definite product of the synthesis.⁷² The latter result assumes a new importance when taken in conjunction with the fact that the chemistry of cellulose is now being attacked by means of enzyme degradation, so that the position has been reached in which, by oppositely directed enzyme actions, the ascent from glucose and the descent from cellulose are being studied. If, and where, such lines of work meet is an interesting speculation.

The value attached to enzyme synthesis of disaccharides is great, and its importance in throwing light on the stereochemical condition of the constituent hexoses is well recognised, but, in the meantime, the inner structure of the disaccharides must be elucidated by methods more familiar to the organic chemist. The structural study of the disaccharides which depends on methylation, followed by identification of the hydrolysis products, has already given improved formulæ for sucrose and lactose. Results equally diagnostic have now been obtained with maltose. The fact that in this case the sequence of reactions outlined above gives tetramethyl glucose as one product has now been confirmed⁷³ under conditions which admit of no dubiety of interpretation, but the research was complicated by an unexpected degradation encountered in the preparation of methylmaltoside, and thus the structure of the reducing glucose component in maltose remained undecided. This, however, has been accomplished by varying the experimental procedure.⁷⁴ Starting from the free sugar, methylmaltoside was produced by the carefully regulated action of methyl sulphate and sodium hydroxide. Thereafter, the same reagents were effective in completing the alkylation, so that the final product was a heptamethyl methylmaltoside. On hydrolysis, the substituted hexoses isolated proved to be tetramethyl glucose and the form of trimethyl glucose which has been obtained

⁷¹ E. Bourquelot and M. Bridel, *Compt. rend.* 1919, **168**, 253; *A.*, i, 137.

⁷² *Ibid.*, 1016; *A.*, i, 361.

⁷³ J. C. Irvine and J. S. Dick, *T.*, 1919, **115**, 593.

⁷⁴ W. N. Haworth and (Miss) G. C. Leitch, *ibid.*, 809.

from methylglucoside. Identification of these methylated sugars affords an experimental verification of Fischer's formula for maltose, which is evidently in good agreement with all the properties of the sugar.

Polysaccharides.

Whilst research on cellulose and its derivatives continues to be exceedingly active, nothing of a very definite nature has been noted dealing with the primary constitution of the most important of all polysaccharides. Our ideas regarding the chemical constitution of cellulose cannot be dissociated from the physical nature of the complex and, at the present time, it is well to preserve an open mind on the general question. Various reviews of past work have been contributed during the year by well-known investigators in this field, but these need not be discussed, and reference may be confined to one experimental result which, although not directly connected with cellulose, has a certain significance. It will be remembered that Pictet obtained *l*-glucosan by the dry distillation of cellulose or starch under diminished pressure, and that he put forward the idea that these polysaccharides arise from the polymerisation of this particular anhydroglucose along different lines. It is now claimed⁷⁵ that, in part, this expectation has been verified as, under the influence of platinum black, glucosan is transformed into an amorphous compound, $(C_6H_{10}O_5)_4$, displaying the properties of a dextrin and in which optical activity is retained. The further expansion of this subject will be watched with great interest, and it may be noted in passing that the chemistry of starch is at present attracting numerous workers. Although in general the results obtained are beyond the scope of this section of the Report, brief reference may be made to the vigorous discussion which has centred round the claim that formaldehyde effects a diastatic degradation of starch. The discussion has, in fact, expanded out of all proportion to the inherent value of the original experimental evidence, but the controversy now appears to be ended. It has been shown, for example,⁷⁶ that the failure of starch to give the iodine reaction after treatment with formaldehyde cannot be accepted as valid evidence of degradation. It has even been found that unchanged starch may be recovered quantitatively after treatment with formaldehyde.⁷⁷ This is damaging evidence, and the idea that the formation of a loose additive compound of formaldehyde and starch would account for all the

⁷⁵ A. Pictet, *Helv. Chim. Acta*, 1918, 1, 226; *A.*, 1918, i, 527.

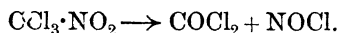
⁷⁶ M. Jacoby, *Ber.*, 1919, 52, [B], 558; *A.*, i, 311.

⁷⁷ W. von Kaufmann and A. Lewite, *ibid.*, 616; *A.*, i, 312.

results described by Woker is supported from other quarters.^{78, 79} At the same time, bio-chemists seem reluctant to abandon the idea that a parallel may be drawn between the action of diastase and that of formaldehyde, but the arguments produced are not convincing, and the subject may be regarded as closed.

Nitrogen Compounds.

So long as discussion is restricted to substances which are essentially open chains, the publications of the past year on aliphatic nitrogen compounds have been less numerous and less complicated than usual. Many of the papers describe new or improved methods of preparing common reagents, and these may be considered in the first place. As is but natural, much attention has been given to the question of utilising, in a profitable manner, the large quantities of organic shell-fillings which have recently been accumulated, and, in the case of chloropicrin, it has been shown⁸⁰ that the compound can be economically employed for the production of methylamine. When reduced by means of iron and hydrochloric acid, exceedingly good yields of the amine salt are obtained, and, as is usually the case in this particular type of reduction, it is possible to restrict the amount of acid to about 3 per cent. of the theoretical quantity. In view of the applications of methylamine it is an important point that, under favourable conditions, only a small proportion of ammonium chloride is formed, and it would appear that the concentration of acid used is an essential factor in controlling the course of the reduction. An explanation of this result is found in another research,⁸¹ where it is shown that chloropicrin is gradually resolved at the boiling point into carbonyl chloride and nitrosyl chloride:



It would thus appear that the formation of methylamine by reduction is due to reaction of chloropicrin as such, whereas ammonia is to be regarded as derived from the decomposition products.

It is perhaps doubtful if the element of danger involved in the preparation and use of chloropicrin will permit of the application of such a method on the large scale. It may be remarked that the reaction between ammonium chloride and formaldehyde, which was recommended by Werner as a convenient source of methylamine,

⁷⁸ H. Sallinger, *Ber.*, 1919, 52, [B], 651; *A.*, i, 253.

⁷⁹ J. Wohlgemuth, *Biochem. Zeitsch.*, 1919, 94, 213; *A.*, i, 361.

⁸⁰ P. F. Frankland, F. Challenger, and N. A. Nicholls, *T.*, 1919, 115, 159.

⁸¹ J. A. Gardner and F. W. Fox, *ibid.*, 1188.

gives good yields of the base, and some modifications of the working details have been contributed in the course of the year.⁸²

Much ingenuity has also been expended on the development of processes for separating primary, secondary, and tertiary amines, but the references for the most part are in the patent literature. As an example, it may be stated that when a mixture of amines is treated with ethyl chloroformate, the tertiary form remains unchanged while the primary and secondary bases are regenerated by hydrolysis.⁸³ Carbonyl chloride may also be employed to separate secondary and tertiary amines,⁸⁴ and in addition considerable success has attended the attempt to develop a practical method of separating amines by partial neutralisation with hydrochloric acid.⁸⁵ Before leaving the subject of amines mention should be made of a substantial improvement in the method for preparing diacetone-amine,⁸⁶ in which the action of ammonia on acetone is greatly facilitated by the addition of calcium chloride. This variation constitutes a distinct advantage, and its adoption not only gives enhanced yields, but reduces the recovery of unaltered acetone and alcohol to a minimum.

Passing to a related subject, a somewhat unexpected property of acetobromoamide is described by Wohl,⁸⁷ who has shown that the compound can function as a brominating agent. The reaction seems to be applicable to a large variety of cases, and the conversion of phenol into *p*-bromophenol may be quoted as a sufficiently striking example of its efficacy. With regard to the mechanism of the change, it would appear that a direct interchange of hydrogen and bromine occurs between the two reacting molecules, and, if this proves to be the case, the prospect is opened out of conducting brominations without the formation of hydrogen bromide as an inevitable and disturbing by-product. Obviously, this would in many cases be a highly desirable condition, particularly when unsaturated or optically active compounds are being manipulated. It may be remarked that, for the time being, research on optically active amino-compounds is in a state of suspension, but there is a distinct revival in the study of general synthetical reactions without reference to stereochemical problems. Most of these investigations have been conducted on standard lines, and are extensions of former

⁸² H. I. Jones and R. Wheatley, *J. Amer. Chem. Soc.*, 1918, **40**, 1411; *A.*, 1918, i, 527.

⁸³ W. Rintoul, J. Thomas, and Nobel's Explosives Co., Ltd., *Brit. Pat.* 127740; *A.*, i, 388.

⁸⁴ *Ibid.*, 128372; *A.*, i, 433.

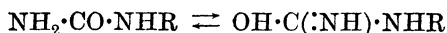
⁸⁵ E. A. Werner, *T.*, 1919, **115**, 1010.

⁸⁶ A. E. Everest, *ibid.*, 588.

⁸⁷ A. Wohl, *Ber.*, 1919, **52**, [B], 51; *A.*, i, 198.

work, so that at present detailed reference is unnecessary, as no points of fundamental theoretical importance appear to be involved. Structural questions, such as the distribution of the nitrogen valencies and the isomerism of the quaternary ammonium salts, still continue to attract workers, but here also is a lack of novelty, although mention may be made in passing of the abnormal salts isolated by Wedekind⁸⁸ in his studies of compounds containing two asymmetric nitrogen atoms of unlike asymmetry. On the other hand, distinct progress has been made in the constitutional problems presented by the carbamides, and some of the outstanding results are now discussed.

It is frequently the case that intimate study of a reaction, generally regarded as simple, reveals many unexpected complications, and much of the recent research on urea furnishes examples of this. In particular, the customary method of expressing the formation of carbamide from carbonyl chloride can no longer be claimed to give a faithful representation of what occurs, as the reaction appears to be based on the union of ammonia and cyanic acid in the keto-imino-form.⁸⁹ In addition, the latest contributions to the study of carbamides not only lend strong support to the views expressed by Werner as to the constitutional changes undergone by these compounds, but also describe new working methods which are of value. In the case of a monosubstituted urea, evidence has been accumulated to show that the equilibrium:



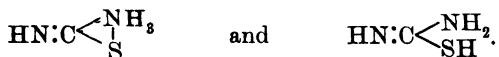
is determined by the electrochemical character of the group R and the co-existence of these forms is confirmed, in the particular example of monomethylurea, by a quantitative study of the reaction with nitrous acid. This can be dissected into two parts, in the second of which nitrosomethylurea is suddenly formed⁹⁰ after the evolution of nitrogen has ceased, and the subsequent conversion of the nitroso-compound into diazomethane by the agency of sodium ethoxide has disclosed the fact that alcohol may be employed as a solvent in the latter reaction. Contrary to expectation, diazomethane reacts with alcohol extremely slowly, if at all, and it is thus possible to effect methylation of a hydroxy-compound by dissolving the latter in an alcoholic solution of nitrosomethylurea and then adding the calculated quantity of sodium alkyl-oxide. This is a distinct advance on the customary method of dissolving, or suspending, a compound in an ethereal solution of the methylating reagent,

⁸⁸ E. Wedekind and T. Goost, *Ber.*, 1919, 52, [B], 446; *A.*, i, 285.

⁸⁹ E. A. Werner, *T.*, 1918, 113, 694.

⁹⁰ *Ibid.*, 1919, 115, 1093.

and advantage has been taken of this useful variation to verify the statement that urea is not affected by diazomethane.⁹¹ Even when dissolved in alcohol and kept in contact with the reagent for many hours the urea remained unchanged, and this result, which is in harmony with the view that urea is to be regarded as possessing the cyclic structure in neutral solution, is in sharp contrast to that obtained with thiourea under parallel conditions. In this case, a methyl group becomes attached to sulphur with the formation of the homologue, $\text{SMe} \cdot \text{C}(\text{:NH}) \cdot \text{NH}_2$, thus adding to the evidence that thiourea exists in neutral solution as an equilibrated mixture of:



A survey of the literature on the use of diazomethane reveals a surprising number of cases where this modified procedure would have proved an advantage, and it is well to direct attention to the method.

In drawing up this Report the original papers have been consulted wherever possible, but before these came to hand copious notes had in many cases been prepared from the abstracts published by the Society. The writer is thus in a position to appreciate the unfailing accuracy of the synopses and, as on a previous occasion, cannot close the Report without expressing his indebtedness to the abstractors.

JAMES COLQUHOUN IRVINE.

PART II.—HOMOCYCLIC DIVISION.

Theoretical.

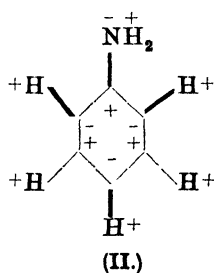
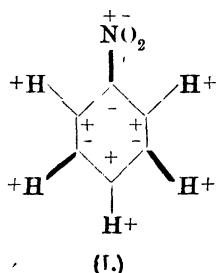
It is extremely difficult to determine the origin and authorship of certain theories in modern organic chemistry, and a reporter may perhaps best note the trend of speculation and emphasise any points on which there seems to be an almost general agreement. During the past year several papers have appeared dealing *inter alia* with the problem of orientation, and the connecting thread is undoubtedly the theory that atoms and groups direct the position in the molecule taken up by entering substituents or, alternatively, determine the constitution of an additive product as the result of a certain effect on alternate atoms in a chain. H. J. Prins¹ dis-

⁹¹ E. A. Werner, *T.*, 1919, 115, 1168.

¹ *Chem. Weekblad*, 1918, 15, 571; *A.*, i, 71.

tinguishes between link-energy and atom-energy and the manner in which the alternating effect is assumed to occur may be gathered from the following quotation²: "The entry of any substituent X into the benzene ring must cause a change in the relation between atom-energy and link-energy,' both in the substituent and in the nucleus. Two cases may arise. In the first, in which the link-energy between X and C₁, the carbon atom to which X becomes attached, is greater than that between C₁ and the hydrogen atom displaced; the atom-energy of C₁ is therefore reduced, and to restore this as far as possible, the link-energy between C₁ and its neighbours, C₂ and C₃, is reduced, with the consequence that the link-energy between C₂ and C₄ and between C₃ and C₅ is increased (C₄ and C₅ being the neighbours of C₂ and C₃ remote from C₁), and that between C₄ and C₆ and C₅ and C₆ is diminished; C₆, therefore, by the diminution of its link-energy, receives an increase of atom-energy, and is therefore rendered more reactive. The effect of introducing X, therefore, is to make the para-carbon atom more reactive. In the second case, in which the link-energy between C₁ and the substituent is less than between C₁ and hydrogen, the redistribution of energy causes an increase in the atom energy of C₄ and C₅, that is, of the carbon atoms in the meta-position."

D. Vorländer³ employs a very similar conception, that of variable internal molecular strain, but uses + and - signs to illustrate the alternating effects of atoms and groups. He definitely states, however, that his views are not based on valency theories. The condition of strain supposed to exist in nitrobenzene (I) and aniline (II) is illustrated below, and it is assumed that reactions will occur in

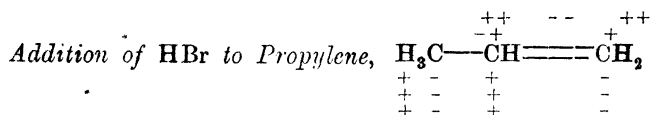


such a manner as to diminish the link tensions so that the *m*-position will be attacked in nitrobenzene and the *o*- and *p*-positions in aniline. The whole theory resembles very much those of Flürscheim and of Thiele. The alternate + - labelling of atoms in a

² Prins, *loc. cit.*

³ *Ber.*, 1919, 52, [B], 263; *A.*, i, 319.

straight chain starting with those of recognised polarity ($\bar{\text{Cl}}$, $\bar{\text{Br}}$, $\bar{\text{I}}$, $\bar{\text{O}}$, $\bar{\text{N}}$, $\bar{\text{S}}$, $\bar{\text{Na}}$, $\bar{\text{H}}$) has also been applied by A. Lapworth⁴ as a means of explaining, and in certain cases of predicting, the direction of chemical changes, such as substitution and addition. Lapworth's views have an electrical basis, and his symbols indicate all the anions and cations which the molecule could conceivably yield. Actual ionisation is neither assumed nor excluded. If as the result of this method of expression an unsaturated centre bears the + sign it will attract the - portion of the molecule added, and vice versa. Also, if a + atom acquires additional + character it becomes more reactive, and similarly - atoms enter into reactions more readily if their - character is enhanced as the result of the influence of the polar atom from which the labelling commences. Exactly similar results are obtained by the application of the present writer's⁵ views on conjugation of partial valencies, primary and secondary. For practical purposes Lapworth's notation is the most convenient, and a few examples may be cited.

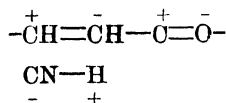


The effect of all the hydrogen atoms is here carried through to the unsaturated carbon atoms, and it is seen that the central atom is overwhelmingly positive, and the result of the reaction is accordingly the production of isopropyl bromide.

Addition of Hydrogen Bromide to Vinyl Bromide and Allyl Bromide.

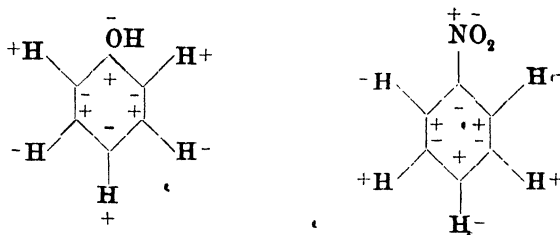


Addition of Hydrogen Cyanide to Unsaturated Ketones.

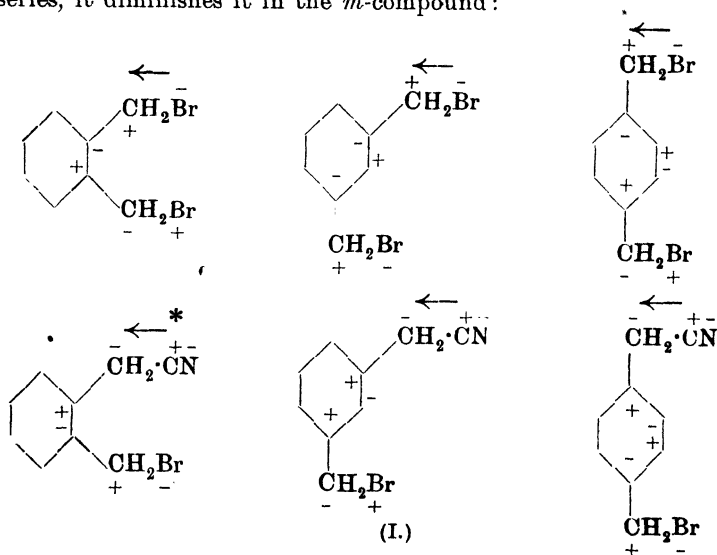


⁴ *Brit. Assoc.*, Bournemouth meeting, Sect. B.

⁵ *Ibid.*

Substitution in the Aromatic Series.

In this connexion mention may be made of a most interesting observation by W. H. Gough and J. F. Thorpe,⁶ who find that although *o*- and *p*-xylylene dibromides react with potassium cyanide in alcoholic solution with the formation of xylylene dicyanides and the intermediate bromo-cyanides cannot be isolated, it is an easy matter to obtain *o*-bromo-*m*-tolylacetonitrile (I) by the interaction of *m*-xylylene dibromide and potassium cyanide. In accordance with the + - rule, the three xylylene dibromides and intermediate bromocyanides would be formulated as shown below, and it is at once evident that, whilst the introduction of the first cyano-group enhances the reactivity of the remaining bromine atom in the *o*- and *p*-series, it diminishes it in the *m*-compound:



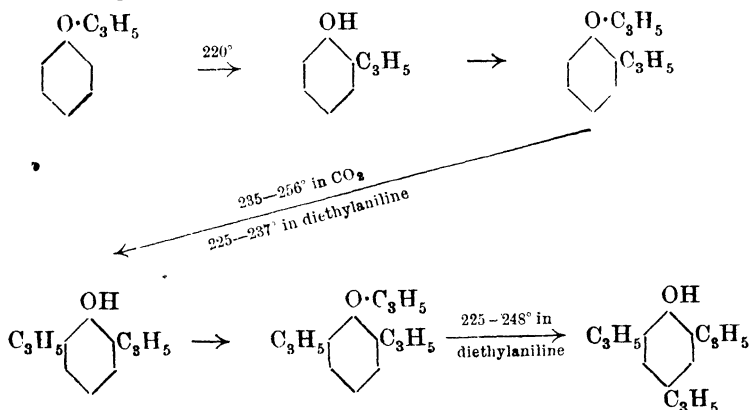
* The arrows indicate the atom from which the labelling commences, in this case the nitrogen.

This work, taken at random to illustrate the application of a

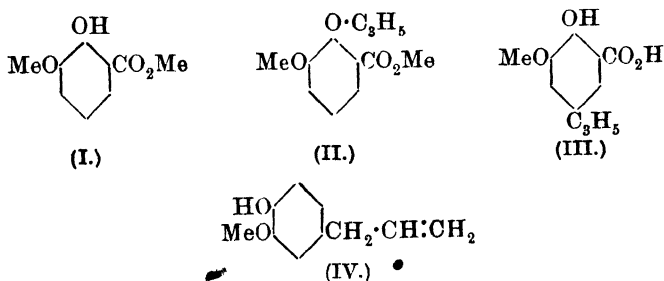
theory, is in itself a matter of considerable importance, and further developments of our knowledge of half-stage reactions in symmetrical compounds will be welcomed. Most synthetical chemists have had sad experiences of poor yields obtained in such processes.

• *Molecular Rearrangement.*

L. Claisen⁷ has continued the investigation of the remarkable transformation of substituted phenyl allyl ethers into allylphenols. The exhaustive allylation of phenol is effected in accordance with the following scheme:



No trace of 4-allylphenol or 2:4-diallylphenol is produced in the transformation of phenyl allyl ether and *o*-allylphenyl allyl ether respectively. 2:4-Diallylphenol is, however, obtained by elimination of the carboxyl group from the product of complete allylation of salicylic acid. A similar device has resulted in a synthesis of eugenol (IV). Methyl guaiacolcarboxylate (I) is converted into its allyl ether (II) by boiling with allyl bromide, potassium carbonate, and a little potassium iodide in methyl ethyl ketone solution. The

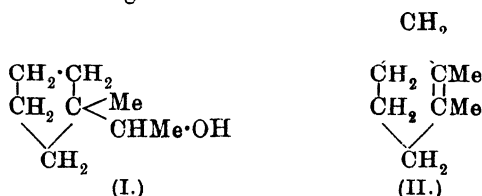


⁷ L. Claisen, O. Eisleb, and F. Kremers, *Annalen*, 1919, **418**, 69; *A.*, i, 266.

acid obtained on hydrolysis of the methyl ester yields *o*-eugenol and carbon dioxide on being heated, but the ester itself is very readily transformed at 230—240° into the methyl ester of 6-hydroxy-5-methoxy-3-allylbenzoic acid (III). The latter yields eugenol when treated with dimethylaniline at 160°:

Pinacone-Pinacolin Transformation.

The dehydrating action of zinc chloride converts 1-methyl-1- α -hydroxyethylcyclopentane (I) into 1:2-dimethyl- Δ^1 -cyclohexene (II), and the reaction is one of the smoothest known enlargements of the cyclopentane ring⁸:



A considerable number of α -glycols containing aryl groups have been synthesised,⁹ and their dehydration products examined. Normal results were observed.

The Action of Benzoic Acid on Arylthiocarbimides.

Becker and Bistrzycki¹⁰ found that the addition of benzoic acid to phenylthiocarbimide did not yield the expected *O*-ester, $\text{NPh} \cdot \text{CS} \cdot \text{O} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, but instead *N*-phenyl-*S*-benzhydrylthiocarbamate- α -carboxylic acid, $\text{NPh} \cdot \text{CO} \cdot \text{S} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$. They assumed at the time that the *O*-ester was the first product, and that this changed over to the substance actually obtained, $\cdot \text{CS} \cdot \text{O} \cdot$ becoming $\cdot \text{CO} \cdot \text{S} \cdot$. In the case of benzoic acid the intermediate product could not be isolated, but the assumption made has now been justified by the study¹¹ of the addition of benzhydrol to phenylthiocarbimide. The reaction is carried out in xylene solution with the sodium derivative of benzhydrol, and results in the formation of *O*-benzhydryl *N*-phenylthiocarbamate, $\text{NPh} \cdot \text{CS} \cdot \text{O} \cdot \text{CHPh}_2$. The transformation to the *S*-ester, $\text{NPh} \cdot \text{CO} \cdot \text{S} \cdot \text{CHPh}_2$, may be accomplished by boiling with acetic acid or by heating at 130—135° or by

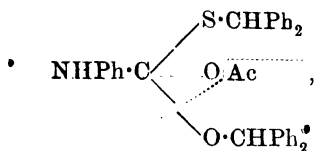
⁸ H. Meerwein, *Annalen*, 1918, **417**, 255; *A.*, i, 162.

⁹ A. Orékhoff, *Bull. Soc. chim.*, 1919, [iv], **25**, 108, 111, 115, 174, 179, 182, 186; *A.*, i, 205, 206, 271, 272.

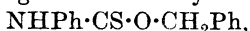
¹⁰ *Ber.*, 1914, **47**, 3149; *A.*, 1914, i, 245.

¹¹ A. Bettschart and A. Bistrzycki, *Helv. Chim. Acta*, 1919, **2**, 118; *A.*, i, 207.

cold hydrochloric acid. The change by acids is regarded as being due to hydrolysis with the formation of benzhydrol, which in the form of an ester adds on to the $\cdot\text{CS}\cdot$ group. The intermediate step may then be written:

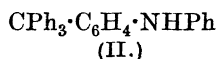
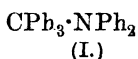


and the reaction is completed as indicated by the dotted line, benzhydrol acetate being eliminated. This hypothesis is strongly supported by the observation that the transformation may be effected by heating the *O*-ester with a little benzhydrol acetate or bromide in toluene. It is interesting that the benzyl derivative,



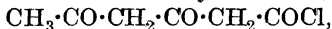
is stable towards boiling glacial acetic acid.

The reaction between chlorotriphenylmethane and diarylamines proceeds normally only in the case of *p*-tetramethyldiaminodiphenylamine. In other cases investigated¹² there is molecular rearrangement, and, for example, chlorotriphenylmethane and diphenylamine yield *p*-anilinetetraphenylmethane (II). The normal product (I) is obtained from tetraphenylhydrazine and triphenylmethyl. It is converted into *p*-anilinetetraphenylmethane by heating with diphenylamine hydrochloride in benzene solution:



New Reactions.

A simple synthesis of phloroglucinol has been described.¹³ Malonyl chloride and acetone in the presence of calcium carbonate yield phloroglucinol and diacetoacetyl chloride,



which can be changed into the trihydric phenol by boiling water in the presence of calcium carbonate.

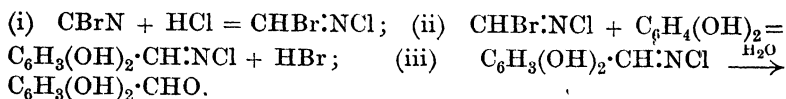
β -Resorcylaldehyde and 2:4:6-trihydroxybenzaldehyde have been obtained¹⁴ by an application of Hoesch's synthesis. Hydrogen chloride is passed into an ethereal solution of resorcinol (or phloroglucinol) and cyanogen bromide in the presence of zinc chloride.

¹² H. Wieland, B. Dolgow, and T. J. Albert, *Ber.*, 1919, **52**, [B], 893; *A.*, i, 324.

¹³ T. Komninos, *Compt. rend.*, 1918, **167**, 781; *Bull. Soc. chim.*, 1918, [iv], 20, 449; *A.*, i, 6.

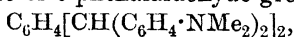
¹⁴ P. Karrer, *Helv. Chim. Acta*, 1919, **2**, 89; *A.*, i, 160.

A crystalline intermediate product containing chlorine but not bromine is collected and boiled with water. The reactions involved appear to be:

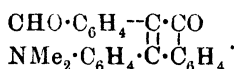


Acetyl chloride and styrene in the presence of stannic chloride give β -chloro- β -phenyl ϵ thyl methyl ketone, which in its turn yields styryl methyl ketone on treatment with diethylaniline.¹⁵

In the course of an investigation¹⁶ of the condensation products of *o*-phthalaldehyde with dimethylaniline both normal and abnormal products were isolated. With excess of dimethylaniline and zinc chloride the leuco-base of *o*-phthalaldehyde green,



was obtained, whilst if the dimethylaniline was restricted to two molecular proportions *o*-aldehydoleucomalachite green was the product. When, however, *o*-phthalaldehyde and dimethylaniline were condensed on the water-bath by means of concentrated hydrochloric acid a red base, $\text{C}_{24}\text{H}_{19}\text{O}_2\text{N}$, was isolated, and convincing evidence is available that this substance must be regarded as 2-*o*-aldehydophenyl-3-*p*-dimethylaminophenylindone:

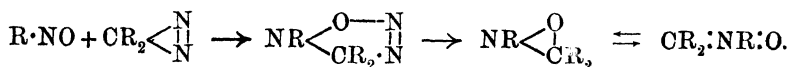


The *N*-alkyloximes have frequently been formulated as cyclic ethers, thus, $\text{R} \cdot \text{CH} - \text{NR}$, but just as the azoxy-compounds are now



regarded as containing the group $\cdot \text{N} : \text{NO} \cdot$, so the substances under consideration may have the constitution $\text{CHR} : \text{NO} \cdot \text{R}$.

H. Staudinger and K. Miescher¹⁷ adopt this view, and also the name 'nitron' first suggested by Pfeiffer.¹⁸ It is now found that 'keto' nitrones, $\text{CR}_2 : \text{NO} \cdot \text{R}$, are readily obtained by the action of aliphatic diazo-compounds on nitroso-compounds, possibly in accordance with the scheme:



The presence of two double linkings in the nitrones is rendered

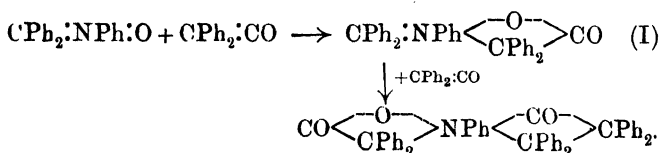
¹⁵ G. Langlois, *Compt. rend.*, 1919, **168**, 1052; *A.*, i, 332.

¹⁶ E. Weitz, *Annalen*, 1919, **418**, 1; *A.*, i, 290.

¹⁷ *Helv. Chim. Acta*, 1919, **2**, 554; *A.*, i, 584.

¹⁸ *Annalen*, 1916, **411**, 72; *A.*, 1916, i, 327.

tolerably certain by the fact that they combine with diphenylketen in two stages, thus:



Diphenyl-*N*-phenylnitrene (from nitrosobenzene and diphenyldiazomethane) is reduced by iron powder to benzophenoneanil, and oxidised by ozone to benzophenone and nitrobenzene. Boiling dilute sulphuric acid hydrolyses it to benzophenone and *p*-aminophenol. By heating the compound (I) at 190° tetraphenyl-*N*-phenylnitrene, $\text{CPh}_2\text{:NPh:CPh}_2$, is obtained, and constitutes the first example of an entirely new type of substance derived from the hypothetical 'nitrene,' $\text{CH}_2\text{:NH:CH}_2$. This compound crystallises in pale yellow prisms melting at 137°. On reduction with aluminium amalgam it yields dibenzhydriylaniline, $\text{NPh}(\text{CHPh}_2)_2$, which was synthesised for comparison. Many other nitrenes and a few nitrenes have been prepared and their properties examined in detail.

Substitution and Orientation.

It is not possible to notice the greater part of the systematic work falling under this head, but it should be stated that there has been considerable activity in this field, and many gaps have been usefully filled.

On iodination¹⁹ with the required quantity of iodine and nitric acid, iodobenzene gives *p*-di-iodobenzene; chlorobenzene gives *p*-chloriodobenzene, and bromobenzene, *p*-bromiodobenzene. *p*-Chloro- and *p*-bromo-toluenes give *p*-chloro- and *p*-bromo-benzoic acids respectively, the methyl groups being oxidised to carboxyl and no entry of iodine taking place. From benzoic acid, *m*-iodobenzoic acid was obtained, and from *o*-phthalic acid, 4-iodo-*o*-phthalic acid. Phenylacetic acid gives *p*-iodophenylacetic acid and cinnamic acid, *p*-iodocinnamic acid.

This method had previously been employed by G. M. Robinson in the iodination of *o*- and *p*-nitroanisole.

The interesting case of the nitration of benzotrichloride has been investigated both by Vorländer^{19a} and by E. Spreckels.²⁰ In the very careful work of the latter precautions were taken to avoid

¹⁹ R. L. Datta and N. R. Chatterjee, *J. Amer. Chem. Soc.*, 1919, **41**, 292; *A.*, i, 153.

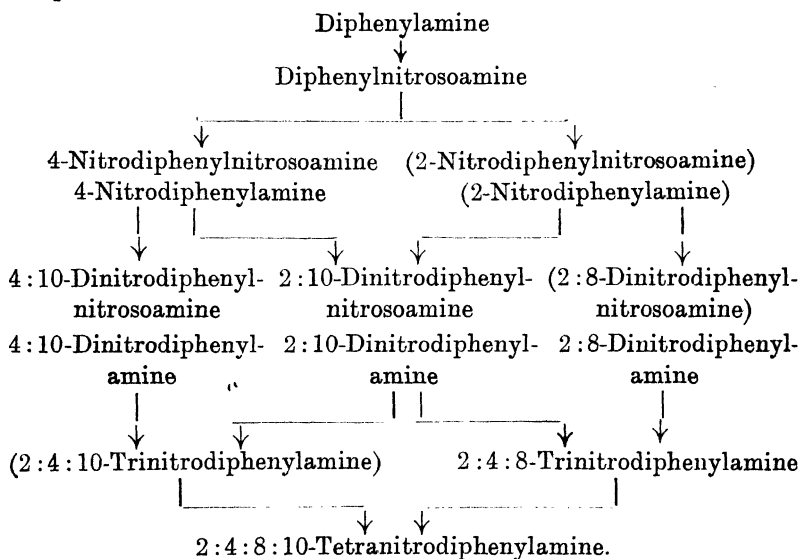
^{19a} *Loc. cit.*

²⁰ *Ber.*, 1919, **52**, [B], 315; *A.*, i, 263.

hydrolysis of the trichloride, and nitrobenzotrichlorides were obtained. Nitrogen pentoxide in carbon tetrachloride at -10° yields as main product *m*-nitrobenzotrichloride with about 20 per cent. of the *p*-derivative and some ortho. Benzoic acid yields a far higher proportion of *m*-nitrobenzoic acid.

The *m*-directive character of the ammonium salt group is already well recognised, but D. Vorländer and E. Siebert²¹ have made a definite contribution to the subject in demonstrating that on brominating phenyltrimethylammonium bromide the *m*-bromo-derivative is obtained, and also that *m*-nitrophenyltrimethylammonium nitrate results from the nitration of phenyltrimethylammonium nitrate. Neither reaction proceeds at all readily, in harmony with the usual experience of *m*-substitutions.

The relations of the nitro-derivatives of diphenylamine have been elucidated,²² and the following scheme²³ illustrates the course of the reaction between nitric acid, nitrous acid, and diphenylamine at the ordinary temperature, and at low concentrations of the interacting compounds :



The compounds shown in brackets have not been isolated, but are probably present in some of the fractions obtained.

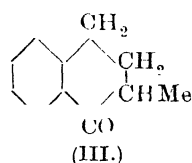
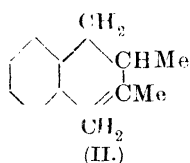
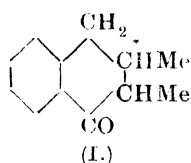
²¹ *Ber.*, 1919, 52, [B], 283; *A.*, i, 320.

²² H. Ryan and T. Glover, *Proc. Roy. Irish Acad.*, 1918, **34**, [B], 97; *A.*, i, 13.

²³ H. Ryan and P. Ryan, *ibid.*, 1919, 34, 212; *A.* i, 482.

Natural Products.

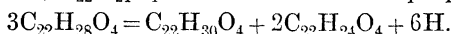
Guaiaretic Acid.—The communication²⁴ under review constitutes a notable advance in our knowledge of the constituents of resins. On dry distillation of guaiacum resin, two substances of unknown constitution are produced, namely, guaiene and pyroguacin or hydroxymethoxyguaiene. Guaiene is now proved to be 2:3-dimethylnaphthalene, which was synthesised by a method that leaves no doubt as to its constitution. β -Phenylisopropyl alcohol was converted into the corresponding bromide and then into ethyl β -phenylisopropylmalonate, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, by condensation with sodiomalonic ester. This was methylated by the usual method, and the dibasic acid obtained by hydrolysis furnished γ -phenyl- $\alpha\beta$ -dimethylbutyric acid, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$, on being heated at 170—190°. Kipping's method was then requisitioned in order to close the naphthalene ring, the acid chloride of the above acid being treated with aluminium chloride so as to obtain 1-keto-2:3-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene (I).



The corresponding alcohol, obtained on reduction, loses water at 200°, yielding the dihydronaphthalene derivative (II), and the dibromide of this is converted into 2:3-dimethylnaphthalene by the action of alcoholic potassium hydroxide. Guaiene was at first thought to be 1:2-dimethylnaphthalene, and the latter substance was also synthesised by somewhat similar methods. The intermediate was, in this case, the ketone (III), and the second methyl group was introduced by the action of magnesium methyl iodide. Guaiaretic acid, the isolation of which from the resin is described, has the formula $\text{C}_{20}\text{H}_{24}\text{O}_4$, is optically active and unsaturated. Its dimethyl ether, $\text{C}_{18}\text{H}_{16}(\text{OMe})_4$, may be reduced under vigorous conditions to a dihydro-derivative, isolated both in an active and inactive form. The latter is thought to be a *meso*-modification, and the conclusion is drawn that the molecule of the hydro-derivative contains two asymmetric carbon atoms symmetrically disposed. Guaiaretic acid methyl ether yields veratric acid on oxidation with potassium per-

²⁴ G. Schroeter, L. Liechtenstadt, and D. Trineu, *Ber.*, 1918, **51**, 1587; *A.*, i, 84.

manganate, and at the same time a portion of the substance is actually reduced to hydroguaiaretic acid methyl ether. The explanation of this quite remarkable transformation is found in the action of Hübl's iodine solution on guaiaretic acid methyl ether, whereby *i*-hydroguaiaretic acid methyl ether and dehydroguaiaretic acid methyl ether, $C_{22}H_{24}O_4$, are obtained in the proportion of 1:2.



It is probable, therefore, that in the permanganate oxidation a portion of the guaiaretic acid methyl ether is reduced at the expense of another portion, and that hydroguaiaretic acid methyl ether is isolated on account of its great stability towards oxidising agents.

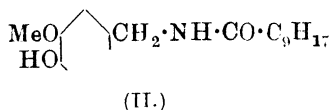
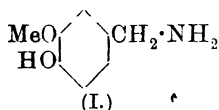
i-Hydroguaiaretic acid methyl ether yields dibromo- and dinitro-derivatives, and the latter on reduction is changed into a diamine, which could not be resolved with the aid of *d*-tartaric acid.

Guaiaretic acid methyl ether must, in view of the above and other evidence, have the constitution



and guaiaretic acid is thus clearly related to eugenol.

Capsaicin.—The pungent principle of cayenne pepper is a substance of general interest on account of its remarkable physiological properties. A great step forward has been made in regard to the elucidation of its chemistry, and, indeed, prior to the investigations of E. K. Nelson²⁵ and of A. Lapworth and F. A. Royle,²⁶ nothing was known beyond the most elementary details. The hydrolysis of capsaicin, $C_{18}H_{29}O_3N$, by means of methyl-alcoholic hydrochloric acid yields 4-hydroxy-3-methoxybenzylamine (I), prepared for com-



parison by the reduction of vanillinoxime. The acid fragment is best obtained by the use of 25 per cent. sodium hydroxide at 180°. It is found to be a new decenoic acid, $C_{10}H_{18}O_2$, yielding by reduction a decoic acid not identical with *n*-decoic acid from coconut oil. Nelson therefore concludes that capsaicin is an amide of the constitution II.

Lapworth and Royle, who made a careful study of the isolation and properties of capsaicin, obtained veratric acid by the oxidation of capsaicin methyl ether. Further, the vigorous reduction of capsaicin by means of sodium and alcohol was found to yield ammonia and a fatty alcohol boiling at 216—217°, and convertible

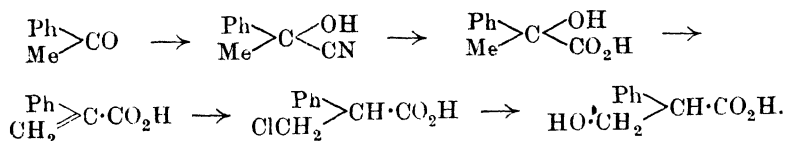
²⁵ *J. Amer. Chem. Soc.*, 1910, **41**, 1115; *A.*, i, 543.

²⁶ *T.*, 1919, **115**, 1109.

by oxidation into *n*-nonoic acid; also the action of inorganic acid chlorides on capsaicin gave a nitrile, which was changed by hydrogen peroxide and dilute sodium hydroxide at 40° into an amide melting at 98—100°, which is the melting point of the amide of *n*-nonoic acid. There is, therefore, still some doubt as to the nature of the fatty chain and its mode of attachment to the vanillylamine molecule. Lapworth and Royle originally suggested a dihydro-oxazole constitution, and, in a note attached to their communication, express the opinion that this possibility is not wholly excluded as the result of Nelson's work on the hydrolysis of capsaicin.

A somewhat allied topic is the pungency of synthetic compounds related to zingerone, and this has been investigated and certain generalisations have been made.²⁷ *o*-Hydroxystyryl methyl ketone was found to be exceptionally pungent.

Tropic Acid and Truxillic Acids.—Although not strictly natural products, it is convenient to mention at this stage that much attention has been paid to these and related subjects during the past year. The preparation of tropic acid has been simplified,²⁸ and the method regarded as most economical is the following. Acetophenone was converted into atrolactic acid by the cyanohydrin method, and the latter, by distillation under diminished pressure, gave atropic acid, which was transformed into β -chlorohydratropic acid by the action of hydrogen chloride in ethereal solution; this, in turn, was hydrolysed by aqueous sodium carbonate, and tropic acid obtained.



Tropic acid has been resolved by H. King²⁹ and also by McKenzie and Wood,³⁰ with almost identical results. The *isoatropic* acids (α and β) are obtained by heating atrolactic acid in an atmosphere of carbon dioxide. Concentrated alkalis convert the α -acid into the β -acid, and it is therefore probable that the isomerism of these dimeric atropic acids is stereochemical. Adequate arguments have been put forward³¹ in favour of the view that the acids have the formula I, and are *cis-trans*-isomerides.

²⁷ (Mrs.) L. K. Pearson, *Pharm. J.*, 1919, **103**, 78; *A.*, i, 489.

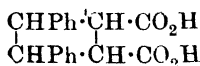
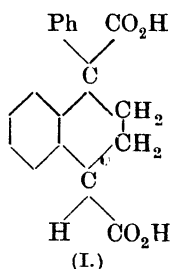
²⁸ A. McKenzie and J. K. Wood, *T.*, 1919, **115**, 828.

²⁹ *Ibid.*, 476.

³⁰ *Loc. cit.*

³¹ L. Smith, *Lunds. Univ. Årsskr.*, 1919, [ii], **14**, 3; *A.*, i, 486.

The truxillic acids (α and β) may also be stereoisomerides having the formula II, since H. Stobbe³² has shown that α -truxillic acid



yields truxone by the action of sulphuric acid only by virtue of initial depolymerisation. The absorption curves of α - and β -truxillic acids exhibit close similarity. Stobbe considers that truxone is $C_{27}H_{18}O_3$, a conclusion reached by a consideration of its relations with truxene and tribenzoylenebenzene, $C_{27}H_{12}O_3$, but R. Stoermer and G. Foerster³³ prepared a methyl ether of the dioxime of α -truxone, and the result of a molecular weight determination in benzene gave the formula $C_{18}H_{12}O_2$ for truxone.

The Naphthalene Group.

R. Weissgerber and O. Kruber³⁴ have performed a remarkable *tour de force* in isolating four pure dimethylnaphthalenes from the heavy oil coal-tar fraction boiling at 260—265°.

1:6-Dimethylnaphthalene is that isomeride which is sulphonated most readily in the cold. Its sulphonic acid was isolated and hydrolysed by steam at 130—140°. The constitution of the liquid hydrocarbon was proved in several ways, for example, by oxidation to the dicarboxylic acid, which was synthesised in stages from β -naphthylamine-5-sulphonic acid.

2:6-Dimethylnaphthalene.—Sulphonation at 135—140° converts the 1:6-isomeride into soluble products and yields a sparingly soluble 2:6-dimethylnaphthalenesulphonic acid. The hydrocarbon obtained on hydrolysis melts at 110—111°, and is identical with the dimethylnaphthalene obtained by Baeyer and Villiger³⁵ from ionone.

2:7-Dimethylnaphthalene.—This new isomeride is isolated by removing as much of the 1:6- and 2:6-isomerides as possible; a

³² *Ber.*, 1919, **52**, [B], 1021; *A.*, i, 329.

³³ *Ibid.*, 1265; *A.*, i, 444.

³⁴ *Ibid.*, 346; *A.*, i, 315.

³⁵ *Ibid.*, 1899, **32**, 2429; *A.*, 1899, i, 921.

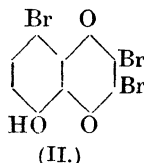
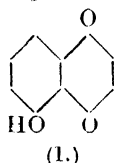
sulphonation at 40° of recovered hydrocarbon then gives a pasty mixture of acids, which is crystallised from 30 per cent. sulphuric acid. On hydrolysis, 2:7-dimethylnaphthalene is obtained (m. p. $96-97^{\circ}$), and its constitution was determined by the usual methods.

2:3-Dimethylnaphthalene (*guaiene*, see above) was obtained³⁶ in relatively small amount from the soluble sulphonic acids accompanying the 2:6-dimethylnaphthalenesulphonic acid.

The results of the work of R. Pummerer and E. Cherbuliez³⁷ on the oxidation of 1-methyl- β -naphthol are of much interest, but the original must be consulted, as the investigation is too complex to be usefully summarised.

An interesting and unexpected observation³⁸ occurs in the Patent literature. 1:6-Dihydroxynaphthalene is condensed with phthalic anhydride in the presence of boric acid to 1:6-dihydroxy-*o*-naphthoylbenzoic acid, which has a very sweet taste. The corresponding 1:5-compound is tasteless.

The action of bromine on juglone (I) in hot acetic acid leads to the formation of a tribromojuglone (II), which is a brilliant red compound, and constitutes, it is claimed,³⁹ a naphthalene dye of a new type.



The substance dyes cotton mordanted with tannin in ecru shades, whilst its indigo-blue sodium salt dyes wool and silk directly.

Very little of importance has been published during the year under review on the chemistry of anthracene, phenanthrene, and higher polynuclear hydrocarbons.

Alicyclic Group.

In 1915, Beesley, Ingold, and Thorpe⁴⁰ showed that a cyclopropane ring in the *spiro*-position with respect to a cyclohexane ring was more readily formed than a simple cyclopropane derivative

³⁶ R. Weissgerber, *Ber.*, 1919, **52**, [B], 370; *A.*, i, 318.

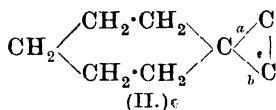
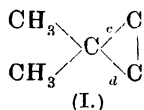
³⁷ *Ber.*, 1919, **52**, [B], 1392, 1414; *A.*, i, 439, 442; R. Pummerer, *Ber.*, 1919, **52**, [B], 1403; *A.*, i, 440.

³⁸ Society of Chemical Industry in Basle, *D.R.-P.* 311213; *A.*, i, 403.

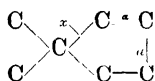
³⁹ A. S. Wheeler and J. W. Scott, *J. Amer. Chem. Soc.*, 1919, **41**, 833; *A.*, i, 490.

⁴⁰ *T.*, 1915, **107**, 1080.

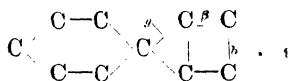
of closely analogous character; also the group II was, when formed, more stable than the group I.



The conclusion drawn was that a part of the strain on the *cyclopropane* ring is taken up by the *cyclohexane* ring, or, in other words, that, owing to the *cyclohexane* valency angle exceeding the normal, the valencies *a* and *b* enclose a smaller angle than the corresponding valencies *c* and *d*. A similar, but far more complex, study has now been published⁴¹ of the valency stabilities in compounds containing the skeletons



and



From the theoretical discussion, it was deduced that the bond *x* should be distinctly more stable than *y*, and a slight increase of stability was anticipated in the case of the bond *a* as compared with *β*. On the other hand, bond *a* should be slightly less stable than *b*, although this effect, being of the third order, might prove incapable of detection. Experimental results justified all these predictions, but this highly interesting paper cannot be adequately condensed, and the reader is referred to the original for details.

A new bicyclic terpene, $C_{10}H_{16}$, which yields pinene nitrosochloride with amyl nitrite and hydrochloric acid, has been discovered⁴² in Finnish turpentine. A new sesquiterpene has been isolated⁴³ from a distillate obtained during the manipulation of pine resin.

Active pinene nitrosochloride has been prepared⁴⁴ from the mother liquors from which the usual inactive compound has separated. By heating with aniline, *d*-pinene was regenerated. By applications⁴⁵ of the method of ozonisation, the formula I is confirmed for *d*-fenchene (Wallach's *D-l*-fenchene), whilst the expression II may be assigned with certainty to *β*-fenchene (Wallach's *D-d*-fenchene and Semmler's *isofenchene*). The fenchene, boiling at 145—147°, is probably III, whilst the fenchene of lowest boiling

⁴¹ C. K. Ingold and J. F. Thorpe, *T.*, 1919, 115, 320.

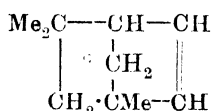
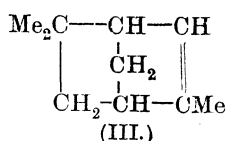
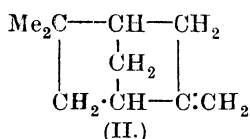
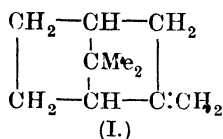
⁴² O. Aschan, *Technikern*, 1918; *A.*, i, 336.

⁴³ O. Aschan, *Finska Kem. Medd.*, 1918; *A.*, i, 338.

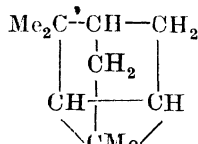
⁴⁴ E. V. Lynn, *J. Amer. Chem. Soc.*, 1919, 41, 361; *A.*, i, 212.

⁴⁵ R. H. Roschier, *Acad. Sci. Fennicae*, 1919, [A], 10, 1; *A.*, i, 408.

point (Semmler's *isoalloylofenchene*) is probably IV mixed with Aschan's β -pinolene (V), the latter in relatively small proportion.

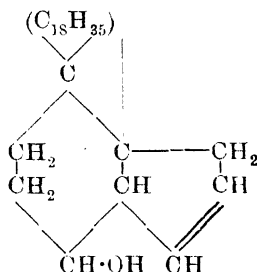


(IV.)



(V.)

The work of Windaus on cholesterol has been continued, and although these investigations cannot yet be usefully summarised, it is considered⁴⁶ that the constitution of cholesterol has been elucidated to the extent indicated in the expression



If this is subsequently confirmed, cholesterol will be the first natural product shown to belong to the *spiro*-ring type.

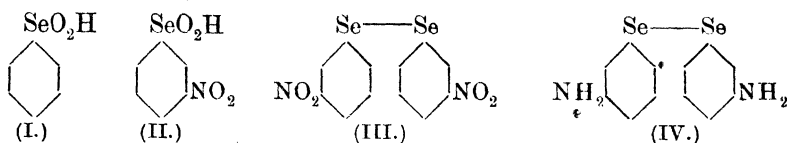
Aromatic Selenium Compounds.

Aniline selenate does not yield the selenium analogue of sulphanilic acid on being heated, but *m*-substituted aromatic selenium compounds can be obtained⁴⁷ from phenylselenious acid (I). Nitration by sulphuric acid and potassium nitrate yields *m*-nitrophenylselenious acid (II), which, on reduction with sodium hydrogen sulphite, becomes di-*m*-nitrophenyl diselenide (III). The corresponding diamine (IV) may also be obtained from *m*-nitroaniline by way of its diazonium derivative and *m*-nitro-

⁴⁶ A. Windaus and O. Dalmer, *Ber.*, 1919, 52, [B]. 162; *A.*, i, 203.

⁴⁷ F. L. Pyman, *T.*, 1919, 115, 166.

phenyl selenocyanate. The latter yields the base (IV) on reduction with tin and hydrochloric acid.



R. ROBINSON.

PART III.—HETEROCYCLIC DIVISION.

THE work of the current year in this field has been somewhat disappointing, and the dearth of interesting material accounts for the brevity of the present Report. No new lines have been opened up on the grand scale of recent researches on chlorophyll and the anthocyanins, but, instead, a good deal of quiet progress has been made in the field of alkaloidal chemistry. The tendency, noted in previous Reports, towards the study of natural rather than synthetic products appears still to hold, which is a matter for congratulation.

On the purely "artificial" side, an interesting example of the benzidine rearrangement in the glyoxaline series may be mentioned, further study of which might help to clarify our ideas concerning the mechanism of that peculiar process. The conversion of isatin into a quinoline derivative is also of interest from the point of view of theory.

Apart from these, the interest in synthetic organic compounds seems to have centred in the coumarin and indole groups, which have given rise to a number of investigations.

The chemistry of natural products is represented by a study of the anthocyanins, with special reference to colour variation in flowers, and a series of important facts have been brought to light in this section of the subject. Steady progress is being made in the examination of the alkaloids, especially in clearing up the constitutions of the more recently isolated members of the group.

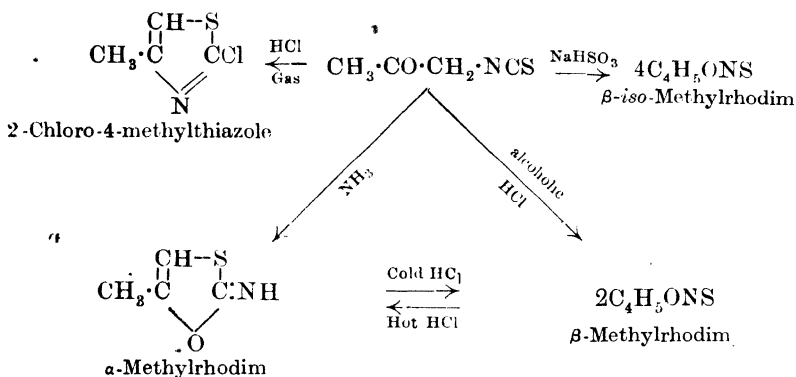
The Rhodim Series.

A study of the reactions of thiocyanacetone¹ has revealed the fact that this substance can give rise to several different heterocyclic compounds according to the reagents employed to produce condensation, and it now seems established that previous investiga-

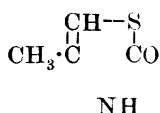
¹ J. Tcherniac, *T.*, 1919, 115, 1071.

tions in this field had led to erroneous conclusions. In an attempt to prepare thiocynoacetone, Hantzsch and Weber² obtained a substance which they supposed to be hydroxymethylthiazole, and at a later date Hantzsch³ believed that he had produced aminomethylthiazole by the action of ammonia on thiocynoacetone. Both these ideas are found to be mistaken.

The reactions with which we are concerned at present are symbolised in the following scheme:

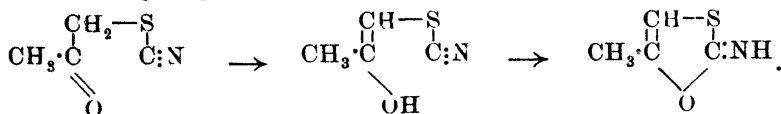


For the compound now termed α -methylrhodim, Hantzsch suggested the structure



which makes it a derivative of thiazole. The properties of the substance, however, do not in any way agree with this formulation. For example, the compound shows no trace of ketonic properties, nor does it behave like an alcohol. Phosphorus pentachloride acts on it without displacing oxygen, which appears to negative the assumption that the oxygen atom exists in the ketonic form or in the enolic structure derivable from the ketone. Hydrolysis of the compound leads to decomposition products, which cannot be derived from such a structure as Hantzsch proposed.

It is now assumed that the condensation reaction takes place in the following stages:

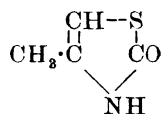


² A. Hantzsch and J. H. Weber, *Ber.*, 1887, **20**, 3127; *A.*, 1888, 256.

³ *Annalen*, 1888, **249**, 7; *A.*, 1889, 413.

and it has been shown that this formulation of the end-product is in agreement with the actual properties of the compound.

With regard to the nature of *isomethylrhodim* and β -methylrhodim, it is too early yet to state that their structures have been definitely established. From the fact that α -methylrhodim and β -methylrhodim are readily interconvertible, it seems reasonable to suppose that the β -compound is a polymericide of the other, and that the structures of the two are similar. On the other hand, *isomethylrhodim* has a chemical behaviour different from either of the other two substances, and it appears to be expressed most satisfactorily as a polymericide of the following:



The Pyrazoline Group.

When phenylhydrazine is allowed to act on phenyl styryl ketone, distyryl ketone, or ethyl γ -keto- $\Delta^{\alpha\alpha}$ -pentadiene- $\alpha\epsilon$ -dicarboxylate, the phenylhydrazones, which are the first products of the reaction, become spontaneously converted into pyrazolines. Further examination shows that the reaction⁴ is a general one unless one of the following conditions is fulfilled, in which case the phenylhydrazone is stable and can be converted into the pyrazoline derivative only by the employment of special processes: (1) The substitution of *p*-nitrophenylhydrazine for phenylhydrazine; (2) the presence of a halogen substituent in the phenyl groups of both ketone and hydrazine; (3) the presence of a methoxy-group in the ortho-position in the ketone.

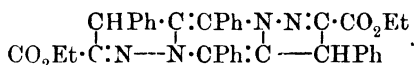
When the pyrazoline derivatives obtained by this reaction were exposed to the influence of Röntgen rays, they exhibited intense fluorescence, not only in the solid state, but also in solution, the intensity of the fluorescence in the latter case being markedly affected by the nature of the solvent. The structural conditions necessary for the production of this Röntgen ray fluorescence appear to be different from those demanded for the power of fluorescing under light rays. For example, if the pyrazoline derivative contains a phenyl or carbonyl radicle in the positions 3 and 5, it fluoresces with Röntgen rays, but fails to do so when these unsaturated groups are displaced by hydrogen atoms or aliphatic groups. Under the action of daylight, however, this substitution

⁴ F. Straus, *Ber.*, 1918, **51**, 1457; *A.*, i, 41.

appears to be insufficient to destroy the fluorescent power, as such compounds fluoresce quite clearly even in diffused daylight.

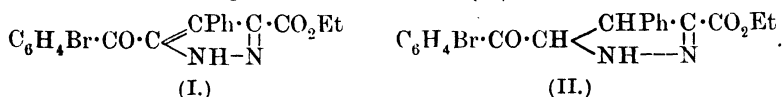
The assumption here made that the pure pyrazoline derivatives are fluorescent may, in the end, prove to be erroneous, as some cases have now been investigated wherein pyrazoline compounds evidently give rise to highly complicated and strongly fluorescent substances,⁵ and it is possible that the phenomena described above may be attributable, not to the pyrazoline derivative, but rather to its products.

It has been shown that ketopyrazolines containing the structure $\text{CO}\cdot\text{CH} < \text{NH}-$, give strongly fluorescent solutions when dissolved in alcohol containing a trace of hydrogen chloride, and the origin of this fluorescence has been traced to the formation of complex materials which resemble in their physical aspect the rhodamine dye. Thus, when hydrogen chloride is passed into boiling methyl alcohol in which ethyl 5-benzoyl-4-phenylpyrazoline-3-carboxylate is suspended, a crimson precipitate is produced which appears to have the composition $\text{C}_{38}\text{H}_{32}\text{O}_4\text{N}_4$. From it two other substances have been obtained which have the compositions $\text{C}_{38}\text{H}_{35}\text{O}_5\text{N}_4\text{Cl}$ and $\text{C}_{38}\text{H}_{36}\text{O}_6\text{N}_4$. The latter is a colourless compound, for which the following structure has been proposed:



Analogous results are obtained with some other pyrazoline derivatives.

An interesting example of solvent effect has come to light⁶ in the pyrazoline series. When *p*-bromophenyl styryl ketone is heated with ethyl diazoacetate, an ester is formed which has the structure (I), but if the reaction mixture is diluted with light petroleum, the end-product is the ester (II):



The Glyoxalines.

A curious abnormality has been detected in the reaction between diazonium salts and the glyoxaline derivatives.⁷ It appears to be established as a general rule that diazonium salts will react only

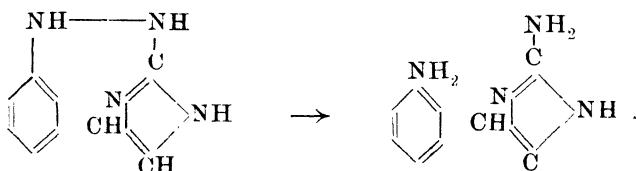
⁵ E. P. Kohler and L. L. Steele, *J. Amer. Chem. Soc.*, 1919, **41**, 1105; *A.*, **i**, 557.

⁶ E. P. Kohler and L. L. Steele, *ibid.*, 1093; *A.*, **i**, 530.

⁷ R. G. Fargher and F. L. Pyman, *T.*, 1919, **115**, 217, 1015.

with those glyoxalines which contain a free imino-group and also a hydrogen atom, or a displaceable group (such as a carboxyl radicle) in the 2-, 4-, or 5-position. Exceptions to this are, however, found in the cases of 5-methylglyoxaline-4-carboxylic acid and glyoxaline-4-carboxylic acid; for although the acids themselves behave normally and couple with diazonium compounds, the esters do not react at all. Up to the present, no definite deductions can be drawn from these results, but it is suggested that the source of the abnormality must be sought in some mutual influence of the imino- and carbonyl radicles.

In the course of this investigation, a most interesting example of the benzidine rearrangement was observed. When 2-benzene-azoglyoxaline was reduced with stannous chloride, the main product was found to be 2-amino-4-*p*-aminophenylglyoxaline, a result which can only be attributed to intramolecular rearrangement of the benzidine type:



It must be admitted that the occurrence of the benzidine change in the case of a five-membered ring is extraordinary, but it is pointed out that the conjugation of the bonds in the glyoxaline ring furnishes a certain parallel to that which is present in the structure of hydrazobenzene.

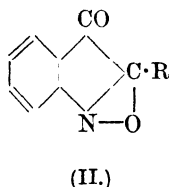
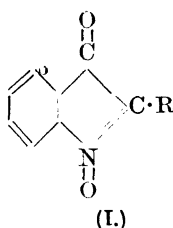
A Synthesis of β -Collidine.

In the course of some synthetic investigations in the quinine series, a mode of forming β -collidine (4-methyl-3-ethylpyridine) has been discovered.⁸ As a first step, 2:6-dihydroxy- β -collidine is prepared, either by heating γ -cyano- β -methyl- α -ethylglutaconimide with hydrobromic acid or by condensing ethyl acetoacetate with ethyl cyanoacetate in the presence of sodium and treating the glutaconic ester thus formed with sodium hydroxide. The next stage in the process consists in converting the dihydroxytollidine into 2:6-dichloro- β -collidine by the action of phosphoryl chloride. Finally, the chlorine atoms are removed by means of hydriodic acid; monochloro- β -collidine is the first product, from which β -collidine is formed at a further stage in the reaction.

⁸ L. Ruzicka and V. Fornasir, *Helv. Chim. Acta*, 1919, 2, 338; *A.*, i, 550.

The Indole Group.

When certain isatogens are heated under pressure with alcoholic hydrogen chloride, they yield less intensely coloured isomerides.⁹ It is suggested that the strongly coloured materials correspond with the structural type (I) containing the pseudo-quinonoid grouping, whilst the new products have the linking (II) within the molecule:



It will be noted that if this view can be substantiated, the change corresponds with the conversion of a five-membered ring into a bicyclic structure containing an extra three-membered ring.

The marked difference in colour between indigotin and its diacetyl derivative has apparently been accounted for by the proof that the latter contains both the acetyl groups attached to the nitrogen atom.¹⁰

A number of substituted indirubins have been prepared by means of three different reactions,¹¹ namely, (1) condensation of isatins with indoxyl acid, (2) condensation of isatins with anilinoisatin, and (3) condensation of isatins in the presence of acetic acid with the technical fusion of phenylglycine. The yield in the last case seems good.

A new and rapid method for extracting indican from indigo-yielding plants has been worked out.¹²

The Coumarin Group.

Among the *cycloparaffins*, it is well known that the stabilities of the five- and six-membered rings approximate closely to one another, for in some cases the five-membered ring can be converted by intramolecular rearrangement into the six-membered type and vice versa. A somewhat similar phenomenon has been noted in the flavone and coumarin series, where the ring contains an oxygen atom in place of one of the methylene groups of the

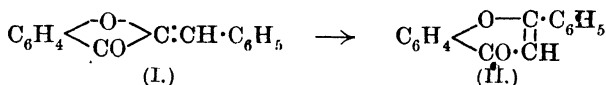
⁹ P. Ruggli, *Ber.*, 1919, **52**, [B], 1; *A.*, i, 221.

¹⁰ D. Vorländer and J. v. Pfeiffer, *ibid.*, 325; *A.*, i, 225.

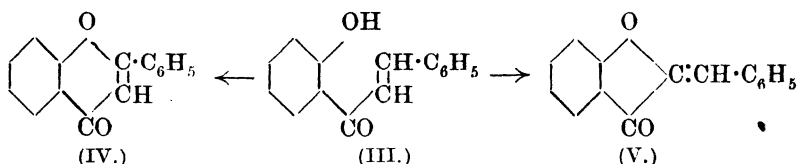
¹¹ J. Martinet, *Compt. rend.*, 1919, **169**, 183; *A.*, i, 457.

¹² B. M. Amin, *Agric. Res. Inst. Pusa, Indigo Publ.*, No. 5; *A.*, i, 283.

cycloparaffin. Thus, when a benzylidenecoumarone of the general structure (I) is treated successively with bromine and potassium hydroxide solution, it may be converted into the corresponding flavanone (II):



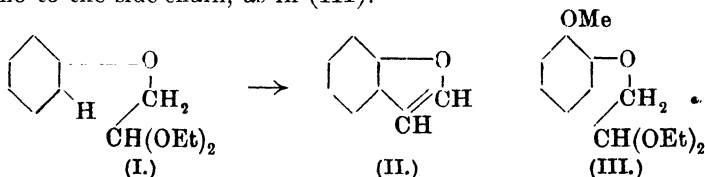
Another branch of the same subject was opened up by the discovery that the removal of hydrogen bromide from substances of the general type (III) may take place in either of two ways, resulting in the one case in the production of a flavone derivative (IV) and in the other in the synthesis of a coumarin compound (V):



During the present year a study has been made¹³ of certain examples of this type with the view of determining the effect of substituents on the course of the reaction.

From the results which have been accumulated, it appears as if the governing factor in the problem is the position of substituents in the phenyl radicle which lies nearest the double bond in the molecule of the type (III). Thus, 2-acetoxyphenyl 4-methoxystyryl ketone dibromide yields a coumaranone derivative when treated with concentrated potassium hydroxide, whereas the isomeric 2-acetoxyphenyl 2-methoxystyryl ketone gives a flavone compound when similarly treated.

This recalls to some extent the phenomena observed in the formation of coumarones from phenoxy-acetals,¹⁴ in which case the influence of substituents is so great that it may inhibit the reaction of coumarone-formation completely. Thus the compound (I) yields the coumarone (II), but no such ring-formation takes place at all if a methoxy-group is inserted into the benzene ring in a position ortho to the side-chain, as in (III).

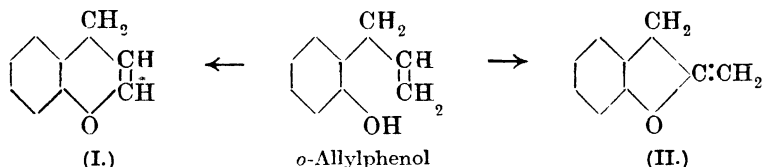


¹³ J. Tambor and H. Gubler, *Helv. Chim. Acta*, 1919, **2**, 101; *A.*, i, 215.

¹⁴ R. Stoermer, *Annalen*, 1900, **312**, 334; *A.*, 1900, i, 650.

A somewhat analogous investigation has been made with regard to the influence of substituents on the stabilities of various coumaranone derivatives. By treating the coumaranone derivative with nitrophenylhydrazine, it is found possible to determine whether or not a rupture of the heterocyclic portion of the molecule has taken place or not under these conditions.¹⁵ It appears that the furan ring of the 1:1-dialkylcoumaranones shows great stability, as in such a case hydrazone-formation occurs without rupture of the ring.

Another example of a similar kind is to be found in some recent work on the *o*-allylphenols.¹⁶ When *o*-allylphenol is submitted successively to acetylation, bromination, and treatment with alcoholic potassium bromide, it might be expected, from analogy to Kostanecki's syntheses, that the parent substance of the flavones, "chromene" (I), would be formed. Actually, however, the reaction takes another course, and a five-membered coumarin ring is produced (II). The reaction appears to be a general one.



Since the coumaranones might be supposed to be capable of enolisation, it is of some interest to find¹⁷ that both chemical and spectrochemical evidence tends to show that they are purely ketonic in nature, there being practically no enolic modification detectable either by measurements of refractive indices or by titration with bromine.

Three new methods for the synthesis of chroman and coumaran¹⁸ have been devised, zinc chloride being used as a condensing agent in each case. In the first method, phenol is condensed with a chlorohydrin, and a poor yield of the required product is obtained. Better results are obtained by using phenyl γ -hydroxypropyl ether (obtained by the action of trimethylene chlorohydrin on sodium phenoxide). When heated with zinc chloride, this compound gives a 30 per cent. yield of chroman. By employing ethylene chlorohydrin and sodium phenoxide, phenyl β -hydroxyethyl ether is formed, and gives a 25 per cent. yield of coumaran on heating with

¹⁵ K. von Auwers and E. Auffenberg, *Ber.*, 1919, **52**, [B], 92; *A.*, i, 218.

¹⁶ R. Adams and R. E. Rindfusz, *J. Amer. Chem. Soc.*, 1919, **41**, 648; *A.*, i, 340.

¹⁷ K. von Auwers, *Ber.*, 1919, **52**, [B], 113; *A.*, i, 230.

¹⁸ R. E. Rindfusz, *J. Amer. Chem. Soc.*, 1919, **41**, 665; *A.*, i, 342.

zinc chloride. The action of zinc chloride on phenyl γ -bromopropyl ether produces a 65 per cent. yield of chroman, whilst the analogous reaction with phenyl β -bromoethyl ether leads to a 30–40 per cent. yield of coumaran.

The Conversion of Isatin into a Quinoline Derivative.

Another example of the change of a five-membered heterocyclic compound into one containing a six-membered ring is furnished by the conversion of indoles into quinoline derivatives. This change is brought about in some cases by the action of nitrous fumes, 2-cyano-2:3-dihydroindole-2-carboxylamide being thus transformed into 2-hydroxyquinoline-3-carboxylamide.¹⁹ It has now been found²⁰ that diazomethane possesses the power of effecting a similar change. When this reagent is allowed to act on isatin suspended in ether, 2:3-dihydroxyquinoline is produced.

A New Heterocyclic Type.

It will be remembered that by means of Skraup's reaction it is possible to fuse a newly formed pyridine ring on to an already existing benzene nucleus. In the case of the formation of quinoline, an aromatic amine is treated with glycerol and sulphuric acid in the presence of an oxidising agent such as nitrobenzene. This reaction has now²¹ been utilised in order to fuse a pyridine ring on to a coumarin nucleus, with the production of a new type of tricyclic compound in which all three rings differ in character, one being a pyrone ring, the central one a benzene ring, and the third a pyridine nucleus.

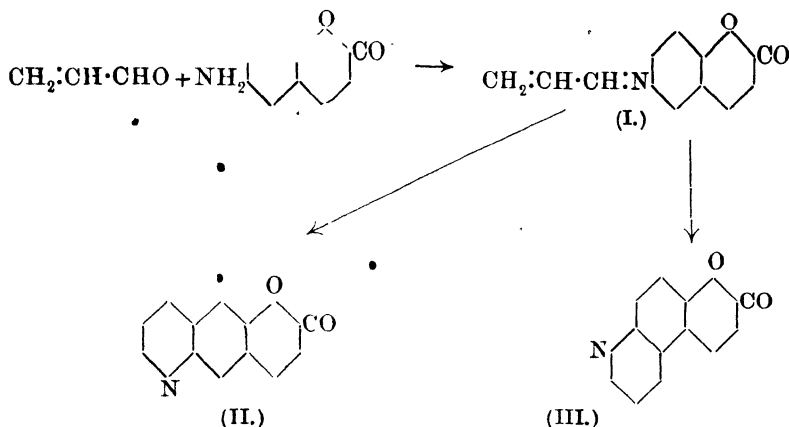
It has been found that the reaction takes place with great readiness, so much so that it is undesirable to utilise aminocoumarins at all, the nitro-derivatives being sufficient; and this naturally simplifies the synthesis considerably.

When 6-nitrocoumarin is treated with glycerol and sulphuric acid in the usual manner, condensation takes place, with the formation of the intermediate compound (I). This might then condense intramolecularly in either of two ways, as shown in the formulæ:

¹⁹ G. Heller and P. Wunderlich, *Ber.*, 1914, **47**, 1617; *A.*, 1914, i, 863.

²⁰ G. Heller, *ibid.*, 1919, **52**, [B], 741; *A.*, i, 283.

²¹ B. B. Dey and M. N. Goswami, *T.*, 1919, **115**, 531.



Conclusive evidence is still lacking as to which of these compounds is produced, but the balance of probability inclines towards (III). Such a substance would logically be termed ψ -1:8-*iso*-naphthoxazone.

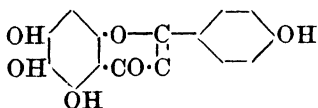
The chemical character of the ψ -naphthoxazones does not differ markedly from that of other quinoline derivatives except in two points. In the first place, the ψ -naphthoxazones dissolve in hot alkali hydroxides, yielding substances of a deep colour, which appear to be unstable acids formed by the opening up of the pyrone ring, since they regenerate the parent naphthoxazone when treated with acids. Secondly, although the ψ -naphthoxazones are colourless and form colourless salts with acids, yet their additive products with alkyl iodides possess deep colours ranging from dark yellow to scarlet-red. When dissolved in water, these ammonium salts lose their colour. From this it would appear that the ions derived from the ammonium salts are colourless, whilst the non-ionised material is coloured. Further investigation of this phenomenon promises interesting results, as the case is evidently the converse of that of phenolphthalein and other indicators, which are colourless in the molecular condition but yield coloured ions in solution.

The Flavone Series.

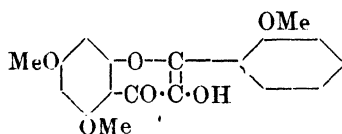
This branch of the heterocyclic compounds has been less worked on recently, but some progress is to be noted. By investigations in previous years, the constitution of scutellarein had been narrowed down to two alternative possibilities, for it might be either 5:7:8:4'- or 5:6:7:4'-tetrahydroxyflavone. It has now²² been

²² G. Bargellini, *Gazzetta*, 1919, 49, ii, 47; *A.*, i, 545.

shown, apparently, that the latter view is the correct one, so that the structure of scutellarein is that shown below (I).



(I)



(II.)

The synthesis of datiscetin appears to have been accomplished,²³ although, on account of the lack of material, it has been impossible to carry out the last step in the process, the demethylation of the trimethyl ether of datiscetin. It seems clear, however, that the synthetic 5:7:2'-trihydroxyflavanol is identical with the trimethyl ether of datiscetin. The formula of the synthetic product is shown above (II).

A number of amino- and azo-derivatives of the flavone series have been prepared, and their properties have been examined. The results show that the amino-group exerts a stronger auxochromic influence than does the hydroxyl radicle.²⁴

The Anthocyanins.

In the earlier stages of the investigation of the anthocyanins, the reduction of quercetin was shown to produce cyanidin, and in this way the genetic relationship between the flavone and anthocyanin series was established.²⁵ In these researches, the reducing agent employed was magnesium and hydrochloric acid, acting in the presence of mercury. A further examination of this field has led to most interesting results.²⁶ Instead of hydrochloric acid, organic acids have been employed to act on the magnesium or zinc which is used in the reduction of the flavone derivative, and in this modification of the method certain complex salts are produced which appear to throw light on the problem of plant colorations.

For example, when myricetin (I) is reduced by this method it yields green-tinted compounds which have the composition



Apparently the reaction proceeds in stages, the phenopyrylium derivative (II) being formed first, and then passing by elimination

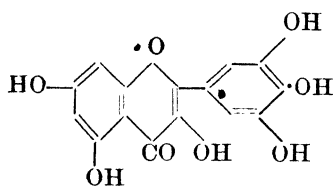
²³ G. Bargellini and E. Peratoner, *Gazzetta*, 1919, **49**, ii, 64; *A.*, i, 547.

²⁴ M. T. Bogert and J. K. Marcus, *J. Amer. Chem. Soc.*, 1919, **41**, 83; *A.*, i, 169.

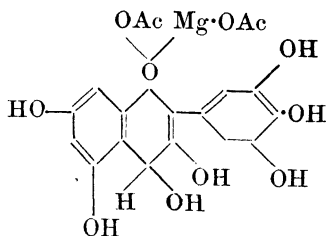
²⁵ *Ann. Report*, 1914, **11**, 138; 1915, **12**, 156.

²⁶ K. Shibata, Y. Shibata and K. Kasiwagi, *J. Amer. Chem. Soc.*, 1919, **41**, 208; *A.*, i, 166.

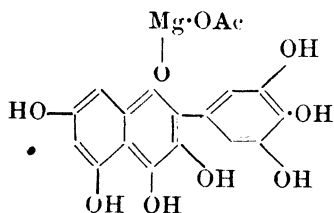
of acetic acid into (III), which finally unites with magnesium acetate to produce (IV). When, instead of myricetin itself, a



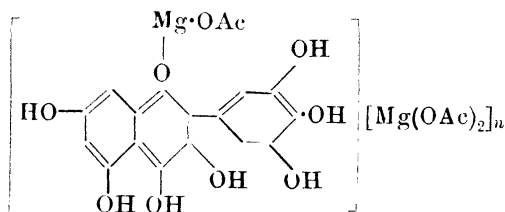
(I.)



(II.)



(III.)



(IV.)

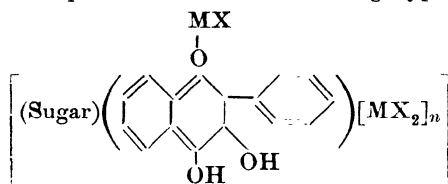
rhamnoside derivative, myricitrin, is employed, the reaction gives rise to a deep blue substance which contains four molecules of magnesium acetate.

It will be remembered that hitherto the reduction of flavone derivatives has always given rise to *red* materials. The apparent anomaly is explained by the fact that when these new green or blue reduction products are treated with hydrochloric acid, they also yield red compounds, the action of the hydrochloric acid bringing about the displacement of the group $\cdot\text{Mg}\cdot\text{OAc}$ by a chlorine atom, with the consequent formation of the red oxonium chloride. It has been proved, however, that even when hydrochloric acid is present, in certain cases a green or blue material may be formed which contains the group $\cdot\text{Mg}\cdot\text{OAc}$ instead of the radicle $\cdot\text{Mg}\cdot\text{OAc}$.

The change of colour induced by the elimination of the magnesium atom from the substances is attributed by the authors to two possible factors. In the first place, the phenopyrylium ring

contains one hydroxyl group more than does the corresponding oxonium salt, and in the second place, the magnesium atom is assumed to take part (by means of auxiliary valencies) in complex-formation. In support of this, it may be pointed out that the reduction of a glucoside (in which one of the hydroxyl groups of the compound is displaced by a sugar molecule) proves that this masking of the hydroxyl tends to shift the absorption band towards the violet, whilst with regard to the other factor, compounds containing the group $\cdot\text{MgCl}$ (which is supposed to be less active than $\cdot\text{MgOAc}$ in complex-formation) have green instead of blue colours.

The authors have thus been led to put forward the following views as to the cause of colour variation in flowers. According to them, metallic complex salts of the following type are important

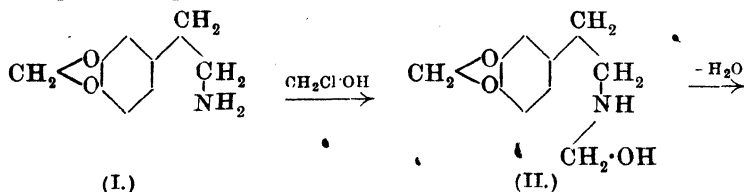


factors in flower coloration and give rise to the "blue" anthocyanins. The metals which they contain are probably calcium and magnesium. The "violet" and "red" pigments are assumed to be complex salts containing fewer hydroxyl groups than the "blue" ones have, or to be mixtures of the "blue" compounds with some red oxonium salts which have been formed from the "blue" compounds by decomposition with acids.

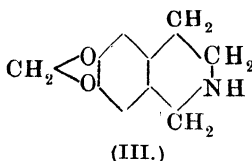
Experiments on the action between natural anthocyanins and solutions of the salts of alkaline earth and heavy metals appear to furnish evidence in support of the authors' contentions.

A New Hydrastinine Synthesis.²⁷

By the action of chloromethyl alcohol on homopiperonylamine (I) in ethereal solution, homopiperonylaminomethanol (II) is formed, and this, when treated with 10 per cent. aqueous hydrochloric acid, yields dihydronorhydrastinine (III), from which hydrastinine itself can be obtained. The following formulæ show the steps in the process:



²⁷ K. W. Rosenmund, *Ber. Deut. pharm. Ges.*, 1919, **29**, 200; *A.*, i, 280.



The Cinchona Alkaloids.

Further progress has been made in this group, but the results are not yet published in full, so that it is impossible to give a complete account of the work which has been carried out.

It has been found²⁸ that, by means of palladous chloride in dilute sulphuric acid solution, it is possible to reduce cinchonine, cinchonidine, and quinine to the corresponding hydro-compounds. Some experiments have been made²⁹ in coupling cinchona derivatives with diazobenzene and reducing the products.

A claim is put forward³⁰ that the cinchona alkaloids can now be built up from quinoline and piperidine compounds. In this form, the claim is possibly correct, but as the material which the authors employed was obtained, not by synthesis, but from the degradation products of the alkaloids themselves, it is evident that the complete synthesis of the cinchona alkaloids is still unachieved.

Some intramolecular changes in cinchonidine have been described,³¹ and the decomposition products of β -hydroxycinchonine have been investigated.³²

Hyoscyne and Oscine.

The complications introduced into the study of alkaloids by the existence of spatial relations are well illustrated in the case of the hyoscines. Hyoscyne occurs in two optically antipodal forms, *d*-hyoscyne and *l*-hyoscyne, and this year an investigation³³ has been made with the object of determining the stereochemical relations of these compounds.

Since the hyoscines are compounds built up from tropic acid and oscine, and since each of the latter occurs in two antipodal forms, it is evident that there are no fewer than eight isomerides possible if racemic and partly racemic varieties are included. These may

²⁸ M. Heidelberger and W. A. Jacobs, *J. Amer. Chem. Soc.*, 1919, **41**, 817; *A.*, i, 493.

²⁹ G. Giemsa and J. Halberkann, *Ber.*, 1919, **52**, [B], 906; *A.*, i, 342

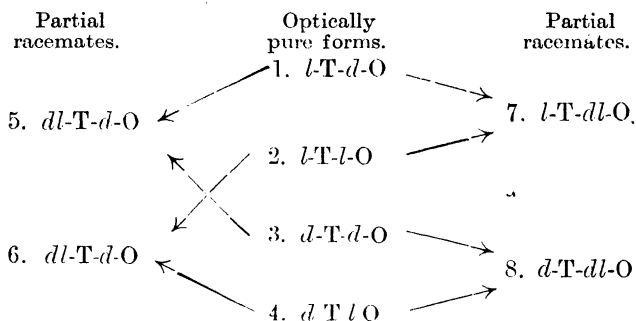
³⁰ P. Rabe and K. Kindler, *ibid.*, 1918, **51**, 1360; *A.*, i, 33.

³¹ E. Léger, *Compt. rend.*, 1919, **169**, 67; *A.*, i, 451.

³² *Ibid.*, 1919, **168**, 404; *A.*, i, 170.

³³ H. King, *T.*, 1919, **115**, 476, 974.

be represented by the following symbols, in which T stands for tropic acid and O for oscine:



Now, when *l*-hyoscine is hydrolysed with either acid or alkali, it yields *l*-tropic and *dl*-oscine. This excludes from the above list all the first six possible structures, since 1—6 contain either *d*-tropic acid or an active form of the oscine, so that for *l*-hyoscine we are left with 7 and for *d*-hyoscine we are driven to choose 8.

When the problem of optically inactive hyoscine is considered, it will be found even more complex. As a starting point, there are four possible varieties of the active forms:

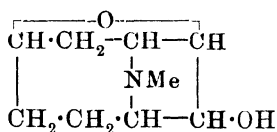
- | | |
|--|--|
| 1. <i>l</i> -tropyl- <i>l</i> -oscine. | 2. <i>d</i> -tropyl- <i>d</i> -oscine. |
| 3. <i>l</i> -tropyl- <i>d</i> -oscine, | 4. <i>d</i> -tropyl- <i>l</i> -oscine. |

Inspection of these will show that 1 and 2 would form an inactive compound when mixed together, as would also 3 and 4. Further, these two inactive mixtures could not be identical with each other, owing to the different mode of linking between the right- and left-handed forms of the acid and base. Finally, a third inactive mixture might be obtained by mixing all four varieties together in molecular proportions, and if combination took place between them this would represent the production of a third possible type of substance in the crystalline form.

Now, if the formation of an ordinary racemic compound be assumed, in which only two molecules combined to form the inactive crystal, it might reasonably be expected that two different types of crystals would be obtained, corresponding with the two pairs (1+2) and (3+4) above. On the other hand, if all four varieties are combined together in one crystal, then no second crystalline compound need be expected. In actual practice, only a single form of the crystalline racemate is known, which may be taken as supporting the combination of the four active forms into one crystal.

King, on the basis of his investigations, suggests that the formula

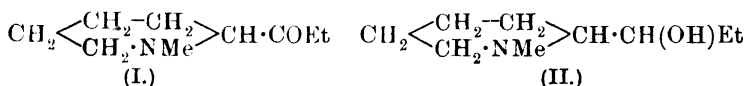
of oscine is allied to that of tropine, and considers that it may have the structure



The Alkaloids of the Pomegranate Tree.

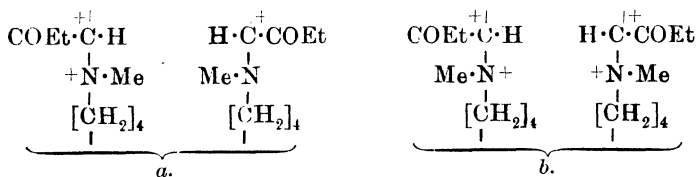
The difficulties which beset investigators in the field of alkaloidal chemistry are well illustrated by this group of compounds. In 1917, researches showed that a reform of the nomenclature was required, whilst this year further facts have come to light which apparently point to an isomerism depending on the spatial arrangement of groups about a tervalent nitrogen atom.

It has been proved³⁴ that methylisopelletierine has the structure (I), and that it can be obtained from conhydrine, which appears to be (II). Closer examination of this reaction, however, shows



that, along with methylisopelletierine, a second base, *dl*-methylconhydrinone, is produced.³⁵ The two bases give different oximes and hydrazones, which excludes the idea that the difference between them is due to keto-enolic desmotropy.

Hess is therefore driven to suggest that the isomerism should be ascribed to a different situation of the methyl group in the compounds in question. If the piperidine ring be supposed to be opened out and then placed in the plane of the paper, the following formulæ illustrate the conception:



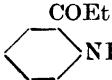
In the formula *b* it will be seen that the methyl radicle is supposed to be spatially adjacent to the carbonyl group, whilst in formula *a* the carbonyl and methyl radicles are on opposite sides of the ring. Steric hindrance is thus assumed to account for the fact that one

³⁴ K. Hess and A. Eichel, *Ber.*, 1917, **50**, 1192, 1386; *A.*, 1918, i, 33, 34.

³⁵ K. Hess, *ibid.*, 1919, **52**, [B], 964; *A.*, i, 345.

compound reacts more readily with semicarbazide than does the isomeric substance.

A suggestion of this kind is not new,³⁶ but the present case appears to be differentiated from previous ones in that the isomerism is still preserved when methyl iodide is added on to each isomeride. Up to the present, it has not been possible to bring about the conversion of methylisopelletierine into *dl*-methylconhydrinone. The methylation of *d*-conhydrinone by means of methyl sulphate produced a mixture of racemic methylisopelletierine and methylconhydrinone.

The occurrence of isopelletierine, , among the pomegranate tree alkaloids has now been established.³⁷

The Areca Nut Alkaloids.

The areca or betel nut contains numerous alkaloids, and it must be confessed that the literature of this branch of chemistry contains an almost equally numerous flock of erroneous observations and deductions. Nearly all the work which was summarised in last year's Report on this subject³⁸ has now been shown to be erroneous.

Taking the results in the order in which they were dealt with last year, the following must be noted. Arecaine was supposed to be definitely proved to be an *N*-methyl derivative of guvacine. This idea seems now to be abandoned. Guvacine appears to be 1:2:5:6-tetrahydropyridine-3-carboxylic acid, and not the 4-carboxylic acid as was supposed last year. This change entails a corresponding alteration in the formula of guvacoline, which is guvacine methyl ester. Arecaidine is the 1-methyl derivative of guvacine, and arecoline is arecaidine methyl ester. The supposed conversion of methylguvacine into the ethyl ester of guvacine by boiling with alcoholic hydrogen chloride turns out to be an error due to the employment of impure materials.

These errors have been frankly admitted by their authors, so it

³⁶ See Ladenburg, *Ber.*, 1893, **26**, 854; 1903, **36**, 3694; *A.*, 1893, **i**, 442; 1904, **i**, 92; but compare Wolfenstein, *ibid.*, 1894, **27**, 2615; *A.*, 1894, **i**, 627. See also Groschuff, *ibid.*, 1901, **34**, 2974; *A.*, 1901, **i**, 745; and Scholtz, *ibid.*, 1910, **43**, 2121; *A.*, 1910, **i**, 634.

³⁷ K. Hess, *Ber.*, 1919, **52**, [B], 1005; *A.*, **i**, 348.

³⁸ *Ann. Report*, 1918, **15**, 107; K. Freudenberg, *Ber.*, 1918, **51**, 1668; *A.*, **i**, 93; K. Hess and F. Leibbrandt, *ibid.*, 1919, **52**, [B], 206; *A.*, **i**, 220; E. Winterstein and A. B. Weinhausen, *Zeitsch. physiol. Chem.*, 1918, **104**, 48; *A.*, **i**, 171.

may be assumed that no further controversy will arise in this particular region of the subject.

The Purine Group.

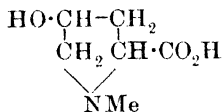
By far the most important work in the purine group during recent years is that done by Johnson and his collaborators, which has now reached the eighty-eighth paper on the pyrimidines.³⁹ It has been impossible to give even the most modest account of the details of this vast investigation from year to year, as the papers do not lend themselves to condensation; but it seems advisable to direct attention here to the extraordinary fertility which this branch of the subject has exhibited in the hands of the investigators, who have made it their own. The work done in this field and in the kindred one of the hydantoins represents one of the most fruitful researches in modern organic chemistry.

Apart from this, the purine group has yielded but little of interest during the current year. Some work has been done on hydurilic acid and α -dimethylhydurilic acid,⁴⁰ but it calls for no particular comment.

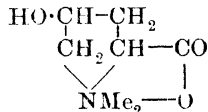
Various Alkaloids.

Our knowledge of cryptopine has been extended considerably during the present year; but the paper⁴¹ on the subject extends to no less than seventy-eight pages, and even a summary of it would be too long for inclusion in this Report. The reader is therefore referred to the Transactions for further information.

The bark of *Croton gubouga* has been investigated,⁴² and from it an acid has been extracted which appears to be 4-hydroxyhygric acid, since on methylation it yields a mixture of betonicine and turicine. The properties of betonicine and turicine have been studied in detail:



• 4-Hydroxyhygric acid.



Betonicine and Turicine.

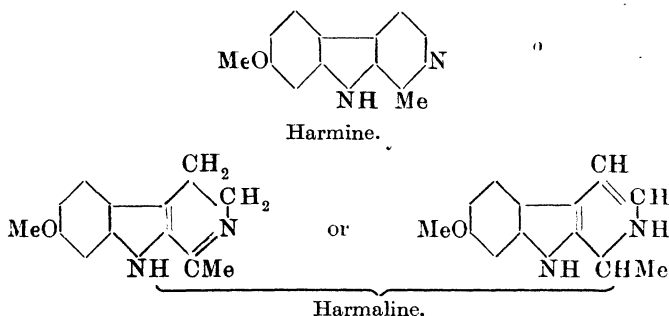
³⁹ T. B. Johnson and I. Matsuo, *J. Amer. Chem. Soc.*, 1919, **41**, 782; T. B. Johnson and L. A. Mikeska, *ibid.*, 810; *A.*, i, 498, 499.

⁴⁰ H. Biltz and M. Heyn, *Ber.*, 1919, **52**, [B], 1298; *A.*, i, 491.

⁴¹ W. H. Perkin, *jun.*, *T.*, 1910, **115**, 713.

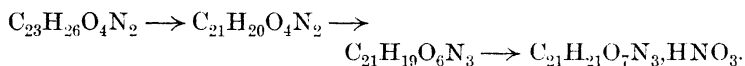
⁴² J. A. Goodson and H. W. B. Clewer, *ibid.*, 923.

Further investigations of the harmine group have led to the conclusion that the structures proposed for harmine in the past are incorrect. It is now suggested⁴³ that the following formulæ represent the compounds better :



The details of the evidence on the matter do not lend themselves to summarisation, and must be consulted in the original paper. Some suggestions as to the possible mode of synthesis of the compounds in the plant are put forward; the details of these are to be found in the Report on Physiological Chemistry in this volume.

A study of the action of nitric acid on brucine⁴⁴ leads to the following results. The steps in the process may be represented as follows :



The last compound is cacotheline. In its general behaviour it resembles the nitroquinones except for the fact that treatment with sulphurous acid changes it into a deep violet or green substance, whereas one would expect a less intensely coloured quinol to be produced in this reaction. It seems now to be established that the violet substance is not a reduction product, but is formed from the cacotheline by isomeric change. This invalidates the previous argument against the nitroquinonoid structure of cacotheline, which therefore seems to be established.

The action of diazonium compounds on various alkaloids has been studied, and it is found⁴⁵ that morphine is the only member of the opium alkaloids which yields a true dye in this way. The reduction of the dye failed to yield any aminomorphine. Methyl- and ethyl-morphine do not give dyes. Curiously enough, the physiological

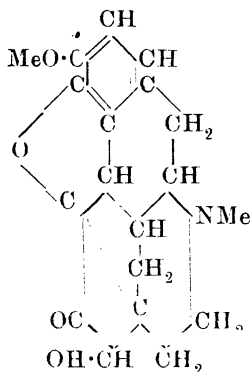
⁴³ W. H. Perkin, jun., and R. Robinson, *T.*, 1919, 115, 933.

⁴⁴ H. Leuchs, *Ber.*, 1918, 51, 1375; *A.*, i, 35.

⁴⁵ L. Lautenschläger, *Arch. Pharm.*, 1919, 257, 13; *A.*, i, 344.

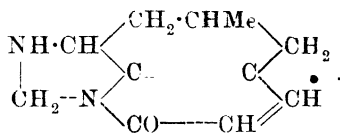
action of morphine is destroyed by the conversion into the colouring matter.

Oxidation of thebaine by means of hydrogen peroxide leads to the elimination of methyl alcohol and the production of a tertiary base which has ketonic properties.⁴⁶ It is supposed that this base is allied to codeinone, which contains one oxygen atom less; and it is therefore termed oxycodeinone. On reduction, it yields oxydihydrocodeinone, which is supposed to have the following structure:

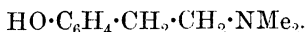


The compound forms a hydrochloride freely soluble in water and sufficiently stable to allow of the solution being sterilised. The hydrochloride serves as a narcotic under the name of eukodal.

The synthesis of cytisoline appears to have been accomplished, and it is thus proved to be 2-hydroxy-6:8-dimethylquinoline.⁴⁷ Assuming this to be correct, Späth⁴⁸ suggests that the most probable formula for cytisine is:



The group of anhalonium or cactus alkaloids⁴⁹ has been examined during the current year.⁵⁰ Anhaline has been shown to be identical with hordenine, so that its formula must be



Mezcaline has been synthesised, and proves to be β -3:4:5-trimethoxyphenylethylamine, $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$. These substances

⁴⁶ M. Freund and E. Speyer, *Münch. med. Woch.*, 1917, **64**, 380; *A.*, i, 345.

⁴⁷ E. Späth, *Monatsh.*, 1919, **40**, 93; *A.*, i, 453.

⁴⁸ *Ibid.*, 15; *A.*, i, 451.

⁴⁹ See also this year's Report on Physiological Chemistry.

⁵⁰ E. Späth, *Monatsh.*, 1919, **40**, 129; *A.*, i, 548.

do not, properly speaking, belong to this section of the Report, as they are open-chain compounds, but it seems well to include them with the rest of the alkaloids.

Miscellaneous.

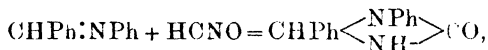
The nitration of 5-diphenyldihydroacridine and the reduction of the nitro-derivatives to amines⁵¹ has led to the discovery of a new class of dyes which have been termed carbazines. The amino-compounds act as leuco-compounds, and yield the dyes by oxidation.

Some further work has been carried out on the methylluric acids.⁵²

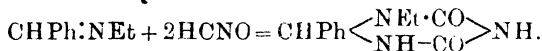
By the condensation of quinolinic acid with various polyhydric phenols, a series of dyes has been prepared which are analogous to the phthaleins.⁵³

Hexacyanogen, $\text{CN}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{C}(\text{CN}) \\ \text{N}:\text{C}(\text{CN}) \end{smallmatrix}\text{N}$, has been obtained by heating a mixture of cyanuric tricarboxylamide and phosphoric oxide in a vacuum to about 250°. ⁵⁴ When passed over a hot platinum wire it decomposes into dicyanogen. Water decomposes it by the elimination of the three cyanogen groups with the production of cyanuric acid. Hexacyanogen appears to be unattacked by chlorine or iodine, and seems to be indifferent towards hydrogen chloride.

Investigation of the action of potassium cyanate on Schiff bases has led to the discovery that the reaction is markedly influenced by the nature of the base used.⁵⁵ Thus benzylideneaniline reacts with potassium cyanate, with the formation of a four-membered cyclic compound:



whilst benzylidene-ethylamine yields a six-membered ring owing to two molecules of isocyanic acid taking part in the process:



The four-membered ring is easily broken down, and yields on hydrolysis a mixture of benzaldehyde and phenylcarbamide; but it has been shown that this reaction cannot be reversed, since these two substances do not condense together to produce any yield of the uretidone from which they are formed.

⁵¹ F. Kehrmann, H. Goldstein, and P. Tschudi, *Helv. Chim. Acta*, 1919, 2, 315, 379; *A.*, i, 551, 552.

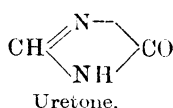
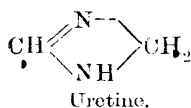
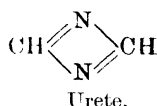
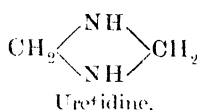
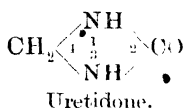
⁵² H. Biltz and M. Heyn, *Ber.*, 1919, 52, [B], 768, 784; *A.*, i, 292, 293.

⁵³ P. C. Ghosh, *T.*, 1919, 115, 1102.

⁵⁴ E. Ott, *Ber.*, 1919, 52, [B], 656; *A.*, i, 260.

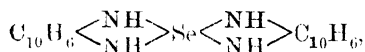
⁵⁵ W. J. Hale, *J. Amer. Chem. Soc.*, 1919, 41, 370; W. J. Hale and N. A. Lange, *ibid.*, 379; *A.*, i, 224.

In view of further developments in this field of research, the following nomenclature for these four-membered ring-systems has been put forward:



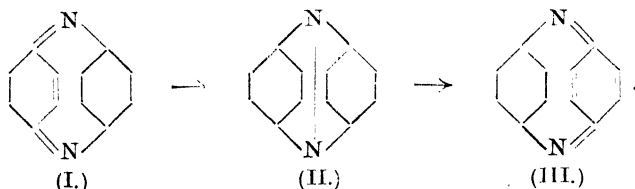
A new method of preparing pyrrole-black has been discovered.⁵⁶ Pyrrole is treated with the calculated quantity of a very dilute ethereal solution of magnesium ethyl iodide, and air is then drawn through the liquid for twenty-four hours. The pyrrole-black is deposited from the solution and exhibits a much more intense tint than is shown by samples prepared by other methods.

A bicyclic selenium heterocyclic compound,⁵⁷



has been obtained by treating two molecules of *perinaphthylenediamine* in pyridine solution with one molecule of selenious acid dissolved in aqueous pyridine. Some reactions of the substance are described.

A new series of compounds, described as parazenes, has been prepared.⁵⁸ Members of the series contain two benzene (or similar) nuclei linked together by two nitrogen atoms, each of which is attached to two para-carbon atoms in the rings. Three possible phases for such a structure are shown below. In the case where one of the phenylene groups contains a substituent, all three phases would be different; but in symmetrically substituted members or in the parent compound the phases (I) and (III) would be identical:



⁵⁶ A. Angeli and A. Pieroni, *Atti R. Accad. Lincei*, 1918, [v], 27, ii, 300; *A.*, i, 134.

⁵⁷ O. Hinsberg, *Ber.*, 1919, 52, [B], 21; *A.*, i, 226.

⁵⁸ A. Angel, *Brit. Pat.* 121347; *A.*, i, 98.

The parazenes are obtained by acting with a condensing agent on benzene or naphthalene derivatives which contain an amino-group and a halogen atom in the para-position with respect to each other and subsequently reducing the hydroxy-parazene thus produced. The members of the series are coloured compounds which yield colouring matters suitable for dyeing.

In concluding this series of Reports on the Heterocyclic Division of Organic Chemistry which have now been written by him for a number of years, the author is again conscious of the limitations which are imposed on a reporter by the nature of the subject, and also by the considerations of space. He is only too well aware that many most interesting subjects have not been dealt with even cursorily in these Reports year by year. This has not been due to any lack of appreciation on his part. Some important papers have defied the process of summarisation altogether; others have been omitted because of limitations in the space which it is possible to allot to the Report. In no case has any paper been left unmentioned without due reason; but it has obviously been impossible to convert the Reports into a mere catalogue of subjects which have been investigated during the year. With this apology, the author brings his work to a conclusion.

A. W. STEWART.

ANALYTICAL CHEMISTRY.

THE transition stage from war to peace during the past year has been indicated in analytical chemistry by the appearance of numerous papers, the previous publication of which had been withheld on national grounds. Most of these communications, however, are concerned with matters of more purely technical importance, and are therefore more suitably dealt with in the Annual Reports of the Society of Chemical Industry. There has also been a number of belated abstracts of papers published two or three years previously in German journals, which, until a few months ago, were not accessible to English readers.

The scarcity of platinum, which was one of the immediate consequences of the war, has been intensified by the continuance of unsettled conditions in Russia. Increasing attention has therefore been given to the preparation of platinum substitutes for analytical apparatus.¹ Comparative tests with alloys containing from 70 to 90 per cent. of gold and 10 to 30 per cent. of palladium (*palau* and *rhotanium*) have shown that in some respects these are superior to platinum for analytical work, but are less suitable for fusions with alkali hydroxides.² In such cases, silver vessels are preferable even to platinum.³ An alloy of nine parts of gold with one part of copper is recommended in place of platinum for cathodes, whilst for anodes the alloy is coated with platinum.⁴ Good results have also been obtained in the electrolysis of gold by the use of an iron anode in place of platinum, whilst platinum gauze is used as the cathode.⁵

Physical Methods.

Solutions of sucrose and mixtures of ethyl alcohol and water have been recommended as suitable standard substances for cali-

¹ Compare *Ann. Report*, 1918, 118.

² L. J. Gurevich and E. Wichers, *J. Ind. Eng. Chem.*, 1919, 11, 570; *A.*, ii, 347.

³ L. Quennessen, *Bull. Soc. chim.*, 1919, [iv], 25, 237; *A.*, ii, 292.

⁴ P. Nicolardot and J. Boudet, *ibid.*, 84; *A.*, ii, 166.

⁵ J. Guzmán, *Anal. Fis. Quím.*, 1919, 17, 115; *A.*, ii, 300.

brating viscosimeters. The method of expressing the results in "centipoises" ⁶ has the advantage that the absolute and specific viscosities thus expressed are the same when compared with water at 20° as the standard.⁷

The "viscosity value" of an oil, Z , may be calculated by means of the formula $Z = 4.072E + 3.518/E$, where E represents Engler degrees. By plotting this value in relation to the temperatures, a series of nearly straight lines is obtained, which cut one another approximately at one point, $Z=1$ and $t=185^\circ$. This is applicable to numerous oils. The viscosity of mixtures of oils is not proportional to the ratio of the constituents, but may be calculated by means of the formula $E_{1+2} = (n_1E_1 + kn_2E_2)/(n_1 + kn_2)$, where E_1 and E_2 represent the respective viscosities of the oils, E_2 being that of the more fluid, n_1 and n_2 their respective proportions, and $k = \sqrt{E_1E_2}$.⁸

A gas pycnometer has been devised consisting of a cylindrical vessel with capillary openings at the ends, closed by means of rubber fittings and screw clips. The vessel is first charged with clean, dry mercury, and gas then drawn into it and weighed. The density is calculated by means of the formula

$$d = \left(\frac{g-p}{V_s} + 1 \right) \frac{1 + 0.00367t}{1 + 0.00367t'} g,$$

in which g represents the weight of the pycnometer, $g-p$ the weight of pycnometer + air, V the volume of the pycnometer, t the temperature at the time of filling, and t' the temperature at the time of weighing, s the density of air in the vessel at t , and d the relative density of the gas (air = 1).⁹

A method of measuring the size of ultramicroscopic particles, such as smoke in air, has been based on the photography of their path in the field of an ultramicroscope, which lies in an alternating electrostatic field. The degree of oscillation gives the data for calculating the diameter of the particles.¹⁰

The following formula may be used for estimating the amount of finely divided material suspended in a liquid from the absorption of light, $1 - I/I_0 = e^{-B/m\beta}$, where I/I_0 represents the coefficient of the transmission of light, m the mass of suspended particles, and

⁶ *Ann. Report*, 1916, 166.

⁷ E. C. Bingham and R. F. Jackson, *Bull. Bureau of Standards*, 1918, 14 59; *A.*, ii, 268.

⁸ E. Oelschläger, *Zeitsch. Ver. Deutsch. Ing.*, 1918, 422.

⁹ K. Kling and L. Suchowiak, *Metan*, 1917, 1, 37; *A.*, 1920, ii, 15.

¹⁰ P. V. Wells and R. H. Gerke, *J. Amer. Chem. Soc.*, 1919, 41, 312; *A.*, ii, 187.

B and β constants which vary with the nature of the particles and wave-length of the light.¹¹

The accuracy of observations in ultra-violet absorption spectroscopy is increased by the use of a new form of spectrophotometer in which four sector-shaped openings are arranged diagonally about the optical axis. The result of this is that all parts of a circular beam of light are utilised in their proper proportion independently of the size of the aperture.¹²

Attention may also be directed to a series of papers on the construction and technical applications of the refractometer.¹³

In a study of the freezing points of solutions, it has been shown that the weight of solvent, W , may be replaced by the expression $w + bw$, where w represents the solute and b a constant varying with the experimental conditions. In the case of a solvent containing several solutes, the observed total depression of the freezing point was found to differ but little from the sum of the calculated depressions for the individual solutes.¹⁴ The limitations of the method as applied to quantitative analysis are discussed. Although under favourable conditions the method will give results accurate within about 2 per cent., previous experience with the same class of substance is necessary.¹⁵

A new method of analysis has been based on the behaviour of substances towards X-rays. A beam of the monochromatic rays is made to pass through a glass tube containing the powdered material, and the resulting diffraction patterns are photographed. The method can be used for the qualitative analysis of mixtures, and in some cases for the approximate estimation of their constituents.¹⁶

Gas Analysis.

Certain precautions should be taken when using cupric oxide for combustions in gas analysis. The temperature must not be allowed to fall below red heat, or the activity of the reduced copper will be diminished. Nitrogen prepared from air by deoxidation with phosphorus invariably contains some phosphorus vapour, and therefore when great accuracy is required, pyrogallate should be used for absorbing the oxygen.¹⁷

¹¹ C. Chéneveau and R. Audubert, *Compt. rend.*, 1919, 168, 766; *A.*, ii, 205.

¹² S. J. Lewis, *T.*, 1919, 115, 312.

¹³ J. C. Philip, F. Stanley, F. Twyman and F. Simeon, H. Main, A. Homer, A. E. Berry, *J. Soc. Chem. Ind.*, 1919, 38, 139-145 *t.*

¹⁴ C. E. Fawsitt, *T.*, 1919, 115, 790.

¹⁵ *Ibid.*, 801.

¹⁶ A. W. Hall, *J. Amer. Chem. Soc.*, 1919, 41, 1168; *A.*, ii, 470.

¹⁷ E. Ott, *J. Gasbeleucht.*, 1919, 62, 89; *A.*, 1920, ii, 52.

The use of soda-asbestos as an absorbent for carbon dioxide has the advantage that it acts as its own drying agent, whilst it enables a more simple form of apparatus to be used. The mixture will absorb upwards of 10 per cent. of its weight of carbon dioxide, and is particularly suitable for the estimation of carbon in steel.¹⁸

A study of the conditions of absorption of oxygen by sodium pyrogallate has shown that the rate of absorption increases with the dilution of the sodium hydroxide solution, but is always proportional to the concentration of pyrogallol in the solution. Carbon monoxide is evolved from all sodium pyrogallate solutions of lower specific gravity than 1.30, and in all cases when the concentration of the oxygen under examination exceeds 95 per cent. A formula is given for the preparation of a rapid absorbent evolving the minimum amount of carbon monoxide.¹⁹

Oxygen in the upper atmosphere may be estimated by means of a simple form of apparatus in which the difference of pressure is measured, with the aid of a barometer tube and micrometer screw, before and after deoxidising the air with phosphorus.²⁰

A sensitive test for ozone is based on the fact that a trace of it immediately destroys the fluorescence of an extremely dilute solution of fluorescein, whereas much larger amounts of nitrous vapour, chlorine, or carbon monoxide are required. As little as 10^{-9} gram of ozone may thus be detected and estimated, so that the reaction is much more sensitive than the starch iodide test.²¹

Carbon monoxide in hydrogen may be estimated by selective oxidation in the presence of a suitable catalyst, and an instrument based on this principle has been devised.²² The reaction is not quite complete between 150° and 400°, whilst the preferential oxidation is reduced by increasing the temperature. Above 400°, the combustion of the hydrogen is more rapid than that of the carbon monoxide.²³

Carbon monoxide may also be estimated by oxidation to carbon dioxide by means of iodine pentoxide under specified conditions. In the case of gases containing more than 0.2 per cent. of carbon monoxide, and where the accuracy need not exceed 0.2 per cent., a modification of the apparatus previously described²⁴ may be used.²⁵

¹⁸ L. J. Rogers, *Canadian Chem. J.*, 1919, **3**, 122.

¹⁹ G. W. Jones and M. H. Meighan, *J. Ind. Eng. Chem.*, 1919, **11**, 311; *A.*, ii, 240.

²⁰ F. W. Aston, *T.*, 1919, **115**, 472.

²¹ L. Benoist, *Compt. rend.*, 1919, **168**, 612; *A.*, ii, 198.

²² E. K. Rideal and H. S. Taylor, *Analyst*, 1919, **44**, 89; *A.*, ii, 200.

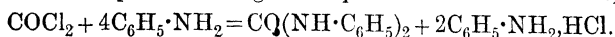
²³ E. K. Rideal, *T.*, 1919, **115**, 993.

²⁴ *T.*, 1914, **105**, 1996.

²⁵ J. I. Graham, *J. Soc. Chem. Ind.*, 1919, **38**, 10π; *A.*, ii, 117.

. Titration with potassium iodate in the presence of hydrochloric acid affords an accurate method of estimating sulphites and sulphur dioxide in gaseous mixtures. An addition of glycerol prevents loss from oxidation of the sulphite by dissolved air, and does not interfere with the subsequent titration.²⁶

A reaction capable of detecting 1 part of carbonyl chloride in 10,000 parts of air depends on the separation of diphenylcarbamide when the air is passed through an aqueous solution of aniline,



The precipitate may be dissolved off the filter with alcohol, the solution evaporated, and the residue dried at 60° and weighed, or ammonia may be separated, as in Kjeldahl's process, and estimated colorimetrically.²⁷

For the estimation of gasoline in natural gas, a measured quantity of the gas is passed through drying tubes and then through an absorption vessel immersed in a mixture of ether and solid carbon dioxide in a drying tube. The vessel is then sealed and the condensed liquid weighed.²⁸ In another method, a solid material, such as charcoal, is used as the absorbent for the gasoline vapours.²⁹

A method of estimating acetylene in admixture with ethylene or other hydrocarbons has been based on the observation of Chavastelon,³⁰ that when acetylene is passed into a neutral solution of silver nitrate, the liquid becomes acid in accordance with the equation: $\text{C}_2\text{H}_2 + 3\text{AgNO}_3 = \text{C}_2\text{Ag}_2\cdot\text{AgNO}_3 + 2\text{HNO}_3$, so that by titrating the liberated nitric acid, a measure of the acetylene is obtained.³¹

Agricultural Analysis.

Few new analytical processes have been published in connexion with agricultural chemistry during the past year, and most of the communications have dealt with methods previously known.

In estimating carbon in soils by the wet combustion method, absorption of the carbon dioxide by barium hydroxide, as in Schollenberger's method,³² has the drawback that carbon dioxide is readily absorbed from the air, whilst absorption in potassium hydr-

²⁶ P. Haller, *J. Soc. Chem. Ind.*, 1919, **38**, 52r; *A.*, ii, 198.

²⁷ A. Kling and R. Schmutz, *Compt. rend.*, 1919, **168**, 773, 891; *A.*, ii, 244.

²⁸ K. Kling, *Metan*, 1917, **1**, 3.

²⁹ G. G. Oberfell, S. D. Shinkle, and S. B. Meserve, *J. Ind. Eng. Chem.*, 1919, **11**, 197.

³⁰ *Compt. rend.*, 1897, **124**, 1364; *A.*, 1897, i, 545.

³¹ W. H. Ross and H. L. Trumbull, *J. Amer. Chem. Soc.*, 1919, **41**, 1180; *A.*, ii, 482.

³² *J. Ind. Eng. Chem.*, 1916, **8**, 427; *A.*, 1916, ii, 395.

oxide solution is tedious. A simple modification, in which the carbon dioxide is absorbed in a soda-lime tube, is rapid and gives accurate results.³³

The total nitrogen in soil extracts cannot be accurately estimated by the direct application of the Kjeldahl process when as much as 10 per cent. of the nitrogen is in the form of nitrates, and in such cases a process of reduction must be used.³⁴ For example, the extract may be rendered slightly alkaline with sodium hydroxide and treated with Devada's alloy, prior to the digestion with sulphuric acid in the Kjeldahl process.³⁵ In another method, the different forms of nitrogen are estimated by using Kjeldahl's method for the total nitrogen other than nitric nitrogen, distilling the ammoniacal nitrogen from the original extract with magnesium oxide, and reducing the residual liquid with magnesium chloride and copper-magnesium alloy to obtain nitric and nitrous nitrogen. Finally, the ammonia and nitrous nitrogen are removed from another portion by boiling with dextrose, ferrous sulphate, and sodium carbonate, and the solution is again reduced with the alloy to obtain the nitric nitrogen.³⁶

Nitrates in soil may be quantitatively extracted with cold water under specified conditions, and may then be accurately estimated in the extract by the phenoldisulphonic acid method, provided the temperature be kept below that at which nitrates and chlorides react with the dilute sulphuric acid. An addition of calcium hydroxide to the soil prior to the extraction will prevent soils containing organic matter from yielding coloured extracts.³⁷

For the estimation of organic phosphorus in soils, it is recommended that calcium should first be extracted with 1 per cent. hydrochloric acid, which is subsequently removed by means of aqueous carbon dioxide solution, after which the organic phosphorus is extracted with 4 to 6 per cent. ammonium hydroxide solution and the extract filtered through a layer of the soil. No advantage is gained by the use of potassium or sodium hydroxide for the extraction.³⁸

The solubility of rock phosphates in 0.2 per cent. citric acid solution is about the same as the solubility in ammonium citrate solution, and although the latter does not extract the whole of the

³³ D. D. Waynick, *J. Ind. Eng. Chem.*, 1919, 11, 634; *A.*, ii, 371.

³⁴ R. S. Snyder, *Soil Sci.*, 1918, 6, 487; *A.*, ii, 295.

³⁵ B. S. Davisson and J. T. Parsons, *J. Ind. Eng. Chem.*, 1919, 11, 306; *A.*, ii, 242.

³⁶ T. Pfeiffer and W. Simmermacher, *Landw. Versuchs-Stat.*, 1918, 93, 65; *A.*, ii, 296.

³⁷ H. A. Noyes, *J. Ind. Eng. Chem.*, 1919, 11, 213; *A.*, ii, 199.

³⁸ C. J. Schollenberger, *Soil Sci.*, 1918, 6, 365; *A.*, ii, 168.

available phosphorus, it is preferable to citric acid as a method of judging the effect of any special treatment of the phosphate. The solubility increases with the strength of the citric acid, whilst dilute nitric acid is still less suitable for the extraction.³⁹

An experimental study of the methods of preparing superphosphates has shown, that in the case of commercial products containing about 12 to 20 per cent. of phosphoric oxide and 10 to 20 per cent. of water there is a system with a fairly high proportion of phosphoric oxide and a very low proportion of water. In estimating free phosphoric acid in such products, it is necessary to use anhydrous ether for the extraction, since water, alcohol, or ordinary ether causes more or less hydrolysis of the monocalcium phosphate, according to the amount of water originally present.⁴⁰

The value of agricultural lime has been shown by practical tests to depend rather on its power of neutralising acids than on the proportions of calcium oxide, magnesium oxide, or carbon dioxide present. The neutralisation power may be estimated by boiling the lime with standard acid, titrating the excess of acid with alkali, and expressing the results in terms of calcium carbonate.⁴¹ An electrical method of estimating the lime requirement of soils has also been devised. The soil is shaken with distilled water and (another portion) with calcium hydrogen carbonate solution for three hours, and the electrical resistance of each liquid determined before and after shaking with the soil. The ratio between the two results affords a measure of the acidity or alkalinity of the soil.⁴²

Organic Analysis.

Qualitative.—A new method of separating and identifying alcohols has been based on their conversion into allophanates, by means of the action of cyanic acid gas. The alcohol is then identified by the melting point of the recrystallised precipitate, and further tests are applied by hydrolysing the allophanate and determining the physical characters of the alcohol. Normal allophanates are produced by alcohols containing an ethinoid group, terpenic alcohols, except linalool, and cyclic alcohols, except terpineol. The presence of the phenolic group in cyclic alcohols interferes with the reaction, and in such cases a preliminary esterification is necessary before applying the test.⁴³

³⁹ J. A. Stenius, *J. Ind. Eng. Chem.*, 1919, 11, 224; *A.*, ii, 199; compare *Ann. Report*, 1917, 151.

⁴⁰ A. Aita, *Annali Chim. Appl.*, 1919, 10, 45; *A.*, ii, 25.

⁴¹ S. D. Conner, *J. Ind. Eng. Chem.*, 1918, 10, 996.

⁴² C. J. Lynde, *Trans. Roy. Soc. Canada*, 1918, [iii], 12, III, 21; *A.*, ii, 376.

⁴³ A. Béhal, *Compt. rend.*, 1919, 168, 945; *A.*, ii, 301.

The detection of methyl alcohol in ethyl alcohol by oxidation to formaldehyde is untrustworthy in the presence of higher alcohols, but the oxidation products of the latter may be distinguished by the fact that they give yellow to reddish-brown colorations with *apomorphine* and sulphuric acid, whereas formaldehyde gives a violet coloration with that reagent.⁴⁴

A specific reaction for oxalates has been described, according to which a red coloration is obtained when the oxalate solution is treated with manganese sulphate solution, acetic acid, and potassium dichromate or alkali hypochlorite solution. The presence of phosphoric or hydrofluoric acid does not interfere with the test.⁴⁵

The distinctive blue coloration given by thiophen in the indophenine reaction is not obtained unless a trace of an oxidising agent, preferably nitric acid, is present; otherwise the coloration is green.⁴⁶

Compounds containing arsenotungstic and arsenomolybdic complexes have been recommended as reagents for phenolic amines. They give an intense blue coloration with phenols, purine derivatives, and phenolic amines. The arsenotungstic reagents also react with hydroxylamine and hydrazine, whilst the arsenotungstomolybdic reagents also give a coloration with substances, such as aniline, containing one amino-group.⁴⁷

A qualitative test for morphine capable of detecting 1 part in 10,000 has been based on its property of yielding dyes on treatment with diazonium compounds, such as diazobenzenesulphonic acid. On adding this compound to an alkaline solution of the morphine salt, colorations ranging from pale to deep red, and changing to orange on acidification, are obtained. The reaction will detect morphine in the presence of other alkaloids.⁴⁸

A comparative study of the sensitiveness of different tests for quinine⁴⁹ has shown that the fluorescence test with sulphuric acid is capable of detecting 1 part in 100,000, whilst the thalleioquinine reaction is ten times less sensitive. In the latter test, it is advantageous to replace chlorine by bromine. Reference is made to a sensitive reaction which has been based on the turbidity given by a solution containing as little as 1 part of quinine in 200,000 with a reagent consisting of potassium iodide and mercuric chloride in acetic acid.⁵⁰

⁴⁴ H. Wolff, *Chem. Zeit.*, 1919, **43**, 558; *A.*, ii, 482.

⁴⁵ H. Caron and D. Raquet, *Ann. Chim. anal.*, 1919, [ii], **1**, 25; *A.*, ii, 438. ⁴⁶ E. Wray, *J. Soc. Chem. Ind.*, 1919, **38**, 837; *A.*, ii, 204.

⁴⁷ L. Guglielmelli, *Anal. Soc. Quim. Argentina*, 1918, **6**, 185; *A.*, ii, 87.

⁴⁸ L. Lautenschläger, *Arch. Pharm.*, 1919, **257**, 13; *A.*, i, 344.

⁴⁹ H. Salomon, *Ber. Deut. pharm. Ges.*, 1918, **28**, 275; *A.*, ii, 87.

⁵⁰ G. Giemsa and J. Halberkann, *Deutsch. Med. Woch.*, 1917, No. 48.

Aconitine, both crystalline and amorphous, gives a violet coloration with phosphoric acid solution containing 4 per cent. of sodium molybdate. Aspidospermine and veratrine also give violet colorations with the reagent, but may be distinguished from aconitine by other tests. The coloration is not given by other alkaloids.

The deep red coloration given by digitalin on treatment with picric acid and potassium hydroxide serves to distinguish it from certain closely allied glucosides, some of which give an orange coloration, whilst others do not give any coloration in the test. Peptones also give a similar red coloration. It is suggested that the reaction may be due to the presence of a carbonyl group linked directly to a carbon atom.⁵¹

Quantitative.—In estimating halogens in organic compounds by catalytic reduction in the presence of palladium, the use of hydrazine is suggested as being preferable to purified hydrogen, being decomposed by the catalyst into nitrogen and hydrogen. After the decomposition, the catalyst is separated by filtration, and the halogen estimated in the filtrate.⁵²

A modification of Young and Swain's method of estimating nitro-groups by means of stannous chloride⁵³ gives trustworthy results with numerous nitro-aromatic compounds. The substance is mixed with alcohol, the air in the flask displaced with carbon dioxide, an excess of standard stannous chloride solution added, and the flask heated on the water-bath while a current of carbon dioxide is passed through it. Finally, the excess of stannous chloride is titrated with standard iodine solution.⁵⁴

A rapid method of estimating methoxyl groups by the methyl iodide process embodies the same principle as that of Kirpal and Bühn,⁵⁵ but instead of evaporating the excess of pyridine, the liquid is diluted with water, acidified with nitric acid, a measured quantity of silver nitrate added, and the excess titrated with thiocyanate.⁵⁶ An analogous method has been devised for estimating methoxyl groups containing sulphur, in which the methyl iodide and hydrogen sulphide are absorbed by pyridine containing silver nitrate, and the silver sulphide separated before completing the estimation.⁵⁷

The presence of water interferes with the accurate estimation of ether in alcohol from the specific gravity of the liquid. This is obviated by fractional distillation and determining the specific

⁵¹ H. Baljet, *Pharm. Weekblad*, 1918, **55**, 457; *A.*, ii, 438.

⁵² M. Busch, *Zeitsch. angew. Chem.*, 1918, **31**, 232.

⁵³ *J. Amer. Chem. Soc.*, 1897, **19**, 812; *A.*, 1898, ii, 186.

⁵⁴ J. G. F. Druce, *Chem. News*, 1919, **118**, 133; *A.*, ii, 199.

⁵⁵ *Ber.*, 1914, **47**, 1084; *A.*, 1914, ii, 497.

⁵⁶ J. T. Hewitt and W. J. Jones, *T.*, 1919, **115**, 193.

⁵⁷ M. Hönl, *Monatsh.*, 1919, **39**, 871; *A.*, ii, 171.

gravity of the alcohol before and after distillation of a first fraction containing all the ether. The amount of the latter is then obtained by means of a formula.⁵⁸

The possibilities and limitations of Duclaux's method of estimating homologous acids by distillation with steam have been studied and the results compared with those previously obtained.⁵⁹ The degree of concentration does not have any pronounced influence on the results, except to some extent in the case of butyric acid. The general conclusion drawn from test distillations was that Duclaux's method will enable the amounts of two fatty acids in a mixture to be estimated within about 1 per cent. of the true quantity, or, in the case of three acids, within about 5 per cent. by a single distillation, or about 1 per cent. by fractional distillation.⁶⁰ In this connexion, mention may be made of a new type of still-head of special construction, by the use of which the distillation slows down when the limit for each pure constituent in a mixture is reached, so that it is possible with the aid of this appliance to separate benzene, toluene, and xylene by direct distillation.⁶¹

Cyanides, cyanates, and bromides may be estimated when in solution together by titrating the liquid with silver nitrate. Titration in alkaline solution gives the amount of cyanide, whilst the three compounds together are obtained by titration in the solution neutralised with acetic acid, and the cyanide and bromide together by titration in the solution acidified with nitric acid.⁶²

A new method of estimating oxalic acid is based on the fact that, when heated with acetic anhydride, it is quantitatively decomposed, so that the volume of carbon dioxide liberated affords a measure of the oxalic acid originally present. Formic acid is the only other organic acid of common occurrence which undergoes a similar decomposition.⁶³

For the estimation of soluble starch in the presence of starch and the products of its hydrolysis, advantage has been taken of the fact that the blue iodine compound with soluble starch is insoluble in a semi-saturated solution of ammonium sulphate. The precipitate is separated and washed with the aid of centrifugal force, dissolved in water and, after removal of the iodine, saccharified, and the resulting dextrose estimated polarimetrically.⁶⁴

There have been a few additions to the methods of analysing

⁵⁸ H. E. Cox, *Analyst*, 1919, **44**, 26; *A.*, ii, 83.

⁵⁹ H. D. Richmond, *ibid.*, 1917, **42**, 125; *A.*, 1917, i, 316.

⁶⁰ *Ibid.*, 1919, **44**, 255; *A.*, ii, 435.

⁶¹ S. F. Dufton, *J. Soc. Chem. Ind.*, 1919, **38**, 45T; *A.*, ii, 136.

⁶² G. Velardi, *Boll. chim. farm.*, 1919, **58**, 241; *A.*, ii, 483.

⁶³ H. Krause, *Ber.*, 1919, **52**, 426; *A.*, ii, 203.

⁶⁴ J. C. Small, *J. Amer. Chem. Soc.*, 1919, **41**, 107; *A.*, ii, 172.

sugars. It has been shown that a cupric sodium hydroxide reagent can replace Fehling's solution, over which it has the advantage of not becoming turbid when boiled.⁶⁵

In order to obtain concordant results in the method of titrating sugars with copper phosphate solution, the exact details of preparing the salt mixture must be followed. The possibility of the reduction of the copper sulphate in the method of Folin and McEllroy⁶⁶ may be prevented by rendering the solution alkaline before adding the thiocyanate, and a modified process embodying this precaution is described.⁶⁷

For the estimation of thiophen in benzene, good results are obtained by a modification of a method in which Denigès' reagent (basic mercuric sulphate) is shaken with the benzene, and the precipitated compound of thiophen dried and weighed. The use of Paolini and Silbermann's reagent (basic mercuric acetate) is also trustworthy, the resulting precipitate, $\text{SC}_4(\text{HgC}_2\text{H}_3\text{O}_2)_4$, being washed with cold water, dried, and weighed.⁶⁸

Sulphonyl chlorides of aromatic substances may be estimated by mixing them with water, neutralising free acids with sodium hydroxide, boiling them under a reflux condenser with excess of sodium hydroxide solution, and titrating the excess. The amount of sulphonyl chloride corresponds with the quantity of alkali used for the hydrolysis.⁶⁹

A convenient method of estimating phenacetin and other *p*-aminophenol derivatives has been based on their reaction with hydrochloric acid and sodium hypochlorite to form *p*-benzoquinone-chloroimide, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2, \text{HCl} + 4\text{Cl} = 4\text{HCl} + \text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NCl}$. After removing the excess of chlorine by a current of air, potassium iodide is added, and the liberated iodine titrated. Four atoms of iodine are liberated in this reaction, and the *p*-aminophenol is regenerated.⁷⁰

A general method of estimating alkaloids is to precipitate the alkaloid from an acidified aqueous solution with alkali, to mix it into a soft paste with plaster of Paris, and to extract the mass with chloroform. The alkaloid is then removed from the extract by means of standard acid, the excess of which is subsequently titrated.⁷¹

⁶⁵ E. Justin-Mueller, *J. Pharm. Chim.*, 1919, [vii], 19, 18; *A.*, ii, 202.

⁶⁶ *J. Biol. Chem.*, 1918, 33, 513; *A.*, 1918, ii, 207.

⁶⁷ O. Folin and E. C. Peck, *ibid.*, 1919, 38, 287; *A.*, ii, 354.

⁶⁸ P. E. Spielmann and S. P. Schotz, *J. Soc. Chem. Ind.*, 1919, 38, 188r; *A.*, ii, 433.

⁶⁹ F. Neitzel, *Chem. Zeit.*, 1919, 43, 500; *A.*, ii, 482.

⁷⁰ A. D. Powell, *Analyst*, 1919, 44, 22; *A.*, ii, 86.

⁷¹ Rapp, *Apoth. Zeit.*, 1918, 33, 463.

From a comparative study of the methods of estimating morphine, a method has been devised in which the alkaloid is extracted by means of a mixture of two parts of chloroform and one part of alcohol. Modifications for use in the cases of preparations of morphine and of opium are also given.⁷²

Experiments have been made which show that berberine may be accurately estimated in an alcoholic extract of *Hydrastis canadensis* by precipitation with Mayer's reagent (mercuric chloride and potassium iodide), and subsequent conversion into berberine picrolonate, which is dried at 100° and weighed.⁷³

Inorganic Analysis.

Qualitative.—Several new indicators have been described in the course of the year. Magenta and other colouring matters of the triphenylmethane group when decolorised with sulphur dioxide may be used as sensitive indicators for the detection of alkalinity, especially in water.⁷⁴ An aqueous decoction of red beetroot is a sensitive indicator for both weak and strong acids. The colour is changed to yellow by alkalis, but is restored by sulphuric acid in a dilution of 1:10,000.⁷⁵

The red iodotannic reaction⁷⁶ is much more sensitive than the starch-iodine reaction, but there must be no excess of either iodine or tannin, or the red coloration will not appear. On the other hand, it has the drawback that potassium iodide interferes with it.⁷⁷ The presence of salts, and especially of potassium iodide, increases the sensitiveness of the starch-iodine reaction, whilst raising the temperature, or the presence of organic substances, such as alcohol, renders it less sensitive.⁷⁸ A convenient method of preparing starch indicator has been based on the property of starch to dissolve in 1 per cent. salicylic acid solution. The preparation keeps well, remains clear, and when diluted gives a deep blue coloration with iodine.⁷⁹

The influence of the quality of, and previous treatment of, the paper on the reactions obtained with coloured test papers has been

⁷² A. Tingle, *Amer. J. Pharm.*, 1918, **90**, 689, 788, 851; *A.*, ii, 87, 88, 175.

⁷³ R. Wasicky and M. Joachimowitz, *Arch. Pharm.*, 1919, **255**, 497; *A.*, i, 564.

⁷⁴ I. Guareschi, *Gazzetta*, 1919, **49**, i, 115; *A.*, ii, 348.

⁷⁵ M. Chauvierre, *Bull. Soc. chim.*, 1919, [iv], **25**, 118; *A.*, ii, 196.

⁷⁶ D. E. Tsakalotos and D. Dalmas, *ibid.*, 1918, [iv], **23**, 391; *A.*, 1918, ii, 454; *Ann. Report*, 1918, 132.

⁷⁷ *Ibid.*, 1919, [iv], **25**, 80; *A.*, ii, 169.

⁷⁸ I. M. Kolthoff, *Pharm. Weekblad*, 1919, **56**, 391; *A.*, ii, 259.

⁷⁹ G. J. Hough, *J. Ind. Eng. Chem.*, 1919, **11**, 767.

studied, and it has been shown that sized papers are less sensitive than unsized, although they give a sharper reaction.⁸⁰

- A new systematic scheme for the detection and approximate estimation of the acids of Group I has been devised, and has been shown by test analyses to be trustworthy.⁸¹

Turning to the reactions for individual substances, it has been found that *o*-tolidine is a delicate reagent for gold, being capable of detecting 1 part in 20 millions. Ferric salts, ruthenium, osmic acid, and vanadium salts also give a yellow coloration, but most other common metals do not give this reaction. In the presence of copper, the coloration is green instead of yellow.⁸²

Mercury in organic or inorganic compounds may be detected by treating the solution or suspension of the substance with nitric acid, excess of ferrous sulphate, and concentrated sulphuric acid so that the liquids do not mix. In the presence of mercury, a reddish-violet ring is formed, and the usual brown ring produced by the nitric acid does not develop until later.⁸³

A sensitive reaction for manganese is based on the red coloration produced when the solution is treated with potassium oxalate, acetic acid, and potassium hypochlorite,⁸⁴ but this test is not so sensitive as that with lead peroxide and nitric acid, although it may be used conversely for detecting traces of oxalic acid.⁸⁵

The difference in behaviour on treatment with excess of mercuric chloride solution affords a means of distinguishing between the sodium salts of different sulphur acids. No precipitate is given by the sulphate, sulphite, or hydrogen sulphite, whereas the sulphide, thiosulphate, and polythionates yield precipitates. Further differentiation is based on the reactions towards methyl-orange and on the behaviour towards iodine.⁸⁶

Several new reagents for micro-chemical analysis have been described. For example, quinosol (the potassium salt of 8-hydroxyquinoline-5-sulphonic acid) and superol (2-hydroxyquinoline sulphate) yield distinctive crystalline precipitates with arsenates, barium, mercurous salts, lead, tin, iron (ferrous), and silver.⁸⁷

Characteristic crystals of lead iodide are obtained by treating soluble lead salts with a drop of potassium bromide and of

⁸⁰ I. M. Kolthoff, *Pharm. Weekblad*, 1919, 56, 175; *A.*, ii, 518.

⁸¹ L. J. Curtman and D. Hart, *Chem. News*, 1919, 119, 25, 37; *A.*, ii, 425.

⁸² W. B. Pollard, *Analyst*, 1919, 44, 94; *A.*, ii, 201.

⁸³ A. Abelman, *Pharm. Zentr.-h.*, 1919, 60, 247; *A.*, ii, 428.

⁸⁴ H. Caron and D. Raquet, *Ann. Chim. anal.*, 1919, [ii], 1, 174; *A.*, ii, 351.

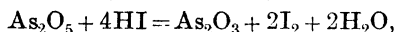
⁸⁵ D. H. Wester, *Pharm. Weekblad*, 1919, 56, 1289; *A.*, ii, 479.

⁸⁶ A. Sander, *Chem. Zeit.*, 1919, 43, 173; *A.*, ii, 241.

⁸⁷ N. Schoorl, *Pharm. Weekblad*, 1919, 56, 325; *A.*, ii, 201.

potassium iodide solution.⁸⁸ A microscopic reaction, which is given by most bismuth compounds, is the formation of colourless, crystalline salts on treatment with dilute hydrochloric acid and hexamethylenetetramine solution.⁸⁹

Quantitative.—Arsenious oxide may be used as a trustworthy standard for iodometry.⁹⁰ The purity of the arsenious oxide may be conveniently estimated by measuring the electrical conductivity of a saturated solution. The most common impurity is arsenic oxide, which may be estimated by determining the reaction of the solution to methyl-orange and methyl-red.⁹¹ In the idiometric estimation of arsenic acid, the reaction,



proceeds from left to right only in strongly acid solution.⁹²

Attention has been drawn to several sources of error, such as atmospheric oxidation, in the estimation of sulphurous acid and sulphites by means of iodine. In order to obtain accurate results, the sulphurous acid solution should be added to the iodine solution.⁹³ The reaction between iodine and thiosulphates varies with the acidity or alkalinity of the solution. In slightly alkaline solution, part of the thiosulphate is converted directly to sulphate, and in strongly alkaline solution the whole of it is thus converted.⁹⁴

For the direct iodometric estimation of hydrogen peroxide, a few drops of ammonium molybdate should be added with the potassium iodide and acid to act as catalyst, and the liberated iodine immediately titrated.⁹⁵

Hypophosphites in sulphuric acid solution are oxidised to phosphorous acid by iodine, and on then adding excess of sodium hydrogen carbonate, the oxidation is continued to phosphoric acid. A method of estimating hypophosphites and phosphites is based on these reactions.⁹⁶ A chromate may be directly estimated by an iodometric method, but it is necessary to have sufficient acid present to inhibit a side reaction.⁹⁷ In using potassium dichromate for iodometric estimations, precautions must be taken to eliminate errors due to impurities in the dichromate and to atmospheric oxidation.⁹⁸

⁸⁸ G. Denigès, *J. Pharm. Chim.*, 1919, [vii], **20**, 159; *A.*, ii, 523.

⁸⁹ *Idem*, *Ann. Chim. anal.*, 1919, [ii], **1**, 213; *A.*, ii, 431.

⁹⁰ R. M. Chapin, *J. Amer. Chem. Soc.*, 1919, **41**, 351; *A.*, ii, 196.

⁹¹ I. M. Kolthoff, *Pharm. Weekblad*, 1919, **56**, 621; *A.*, ii, 522.

⁹² *Ibid.*, 1322; *A.*, ii, 427.

⁹³ *Ibid.*, 1366; *A.*, ii, 473.

⁹⁴ *Ibid.*, 572; *A.*, ii, 365.

⁹⁵ *Ibid.*, 949; *A.*, ii, 370.

⁹⁶ Boyer and Bauzil, *J. Pharm. Chim.*, 1918, [vii], **18**, 321; *A.*, ii, 77.

⁹⁷ I. M. Kolthoff and E. H. Vagelenzang, *Pharm. Weekblad*, 1919, **56**, 514; *A.*, ii, 300.

⁹⁸ C. R. McCrosky, *J. Amer. Chem. Soc.*, 1918, **40**, 1662; *A.*, ii, 31.

The abnormally high results obtained when sodium arsenate is used for titrating potassium permanganate in the presence of nitric acid are probably due to the occurrence of complicated reactions in the course of the titration.⁹⁹

A volumetric method of estimating sulphurous acid has been based on the oxidation of the sulphur dioxide by means of hydrogen peroxide, and titration of the excess of hydrogen peroxide by means of potassium permanganate solution, standardised against pure hydrogen peroxide under similar conditions.¹

For the volumetric estimation of sulphates, a method sufficiently accurate for technical purposes has been based on the reaction between certain soluble sulphates and freshly precipitated barium oxalate, and titration of the resulting soluble oxalate with permanganate solution.²

An oxidimetric method has been devised to obviate the sources of error in the ordinary methods of estimating nitrous acid and nitrites. The nitrite solution is run into excess of acidified permanganate solution, the excess reduced by means of ferrous sulphate, and the excess of the latter titrated with standard permanganate solution. Chlorides or bromides in small quantity do not interfere with the process.³ The influence of fluorides on the oxidimetric estimation of nitrites may be eliminated by combining an iodometric method with the oxidimetric method.⁴

A cyanometric method of estimating silver and halogens has been based on the fact that silver iodide in cold, very dilute ammoniacal solution forms only a turbidity unless a large excess of potassium iodide was added. On adding potassium cyanide, the turbidity disappears when sufficient CN' has been added to form $\text{Ag}(\text{CN})_2'$. Halogens are estimated indirectly by adding excess of silver nitrate, removing the precipitate, and titrating the excess of silver.⁵

The behaviour of various metallic ferrocyanides towards chlorine and bromine has been studied, and it has been shown that nickel and bismuth are quantitatively precipitated as ferrocyanide.⁶ The conditions under which zirconium is quantitatively precipitated as phosphate have been investigated; the separation is complete in the presence of 2 to 20 per cent. of sulphuric acid. The addition of a small quantity of ammonium nitrate to the

⁹⁹ A. Bose, *Chem. News*, 1918, **117**, 369; *A.*, ii, 36.

¹ T. J. I. Craig, *J. Soc. Chem. Ind.*, 1919, **38**, 967; *A.*, ii, 241.

² A. C. D. Rivett, *Chem. News*, 1919, **118**, 253; *A.*, ii, 295.

³ J. S. Laird and T. C. Simpson, *J. Amer. Chem. Soc.*, 1919, **41**, 524; *A.*, ii, 242.

⁴ I. Bellucci, *Gazzetta*, 1919, **49**, i, 209; *A.*, ii, 476.

⁵ J. Eggert and L. Zepfel, *Ber.*, 1919, **52**, [B], 1177; *A.*, ii, 351.

⁶ F. F. Werner, *Zeitsch. anal. Chem.*, 1919, **58**, 23; *A.*, i, 313.

washing water prevents hydrolysis of the precipitate, which will then, on ignition, yield zirconium pyrophosphate.⁷ The composition of the precipitate approximates more closely to the normal phosphate as the acidity of the solution increases.⁸ The method effects a separation of zirconium from aluminium, iron, and chromium.⁹

A simple method of estimating carbon dioxide in carbonates is to treat the substance with acid in a test-tube placed in a suction flask, and to absorb the carbon dioxide in standard barium hydroxide solution. The resulting barium carbonate is separated, and the excess of alkali in the filtrate titrated.¹⁰

Perchlorates may be estimated in the presence of chlorate by a method based on the fact that only the perchlorates are reduced by a hot acid solution of titanium chloride, the excess of which is subsequently titrated with ferric chloride solution.¹¹

An accurate method of estimating arsenic acid is by reduction with potassium thiocyanate, and gravimetric estimation of the arsenic as sulphide.¹²

A combination of the Rose-Finkener and Eschka methods affords a rapid and accurate means of estimating mercury in most of its compounds. The powdered substance is heated with iron powder in a porcelain crucible covered with a gold or silver crucible, through which circulates cold water, and the condensed mercury is washed with alcohol and weighed.¹³

The fact that gallium chloride volatilises at a relatively low temperature enables gallium to be separated from other metals the chlorides of which are less volatile.¹⁴

Molybdenum may be estimated by precipitation as sulphide, and conversion of the sulphide into molybdenum trioxide, but the temperature should not be allowed to exceed about 425°, or the molybdenum trioxide will sublime.¹⁵

A study of the methods of estimating calcium has shown that precipitation as oxalate from a solution acidified with acetic acid in the presence of excess of ammonium chloride gives accurate

⁷ G. E. F. Lundell and H. B. Knowles, *J. Amer. Chem. Soc.*, 1919, **41**, 1801; *A.*, 1920, ii, 60.

⁸ G. Steiger, *J. Washington Acad. Sci.*, 1918, **8**, 637; *A.*, ii, 82.

⁹ P. Nicolardot and A. Reglade, *Compt. rend.*, 1919, **168**, 348; *A.*, ii, 171.

¹⁰ D. D. van Slyke, *J. Biol. Chem.*, 1918, **36**, 351; *A.*, ii, 78.

¹¹ J. G. Williams, *Chem. News*, 1919, **119**, 8; *A.*, ii, 348.

¹² L. W. Winkler, *Zeitsch. angew. Chem.*, 1919, **32**, I, 122; *A.*, ii, 243.

¹³ S. Piña de Rubies, *Anal. Fis. Quim.*, 1918, **16**, 661; *A.*, ii, 80.

¹⁴ T. W. Richards, W. M. Craig, and J. Sameshima, *J. Amer. Chem. Soc.*, 1919, **41**, 131; *A.*, ii, 157.

¹⁵ K. Wolf, *Zeitsch. angew. Chem.*, 1918, **31**, I, 140; *A.*, ii, 121.

results. The precipitate is best weighed as oxalate.¹⁶ Good results may also be obtained by precipitating the calcium from an ammoniacal solution and weighing it as oxide.¹⁷

Electrochemical Analysis.

There have been several important contributions to the methods of electrometric titration during the year. A special form of potentiometer has been devised for determining the end-point sharply in such titrations, a calomel electrode being used.¹⁸ By means of this instrument, ferrous iron may be accurately estimated by titration with potassium dichromate or permanganate, and ferric iron and potassium dichromate by titration with stannous chloride. Advantages of the method are that extremely dilute solutions may be used, that the time is greatly reduced, and that some of the conditions may vary within fairly wide limits.¹⁹

It has been shown in titrating ferrous salts with potassium permanganate solution in acid solution that the conductivity remains fairly constant throughout the titration, but that if insufficient acid is present, the conductivity steadily falls until the oxidation is complete before becoming constant, the end-point being indicated by a sharp change in the direction of the curve. On the other hand, in titrating manganous salts with permanganate, the electrical conductivity increases until the oxidation is complete, and then becomes constant.²⁰

When potassium dichromate is used for titrating ferrous iron in acid solution, the *E.M.F.* increases rapidly towards the end-point, which may be obtained from the middle point of the curve section. Titration with potassium bromate solution also gives good results. When potassium permanganate is used, the *E.M.F.* is increased by stirring the solution during the titration.²¹

From a study of the methods of estimating sulphates, chlorides, calcium, and magnesium in relatively weak solution by measurement of the electrical conductivity, it has been found that down to a certain limit of dilution the results are accurate to within about 1 per cent., but that beyond that limit smooth curves are obtained, and the results are no longer trustworthy.²²

Ferrocyanides may be estimated by slow titration with potassium

¹⁶ I. W. Winkler, *Zeitsch. angew. Chem.*, 1918, 31, I, 187, 203; *A.*, ii, 34.

¹⁷ E. Canals, *Bull. Soc. chim.*, 1918, [iv], 23, 422; *A.*, ii, 34.

¹⁸ H. S. Roberts, *J. Amer. Chem. Soc.*, 1919, 41, 1358; *A.*, ii, 471.

¹⁹ J. C. Hostetter and H. S. Roberts, *ibid.*, 1337; *A.*, ii, 480.

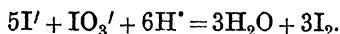
²⁰ V. Villumbræles, *Anal. Fis. Quim.*, 1919, 17, 100; *A.*, ii, 299.

²¹ I. M. Kolthoff, *Chem. Weekblad*, 1919, 16, 450; *A.*, ii, 352.

²² G. A. Freak, *T.*, 1919, 115, 55.

permanganate in acid solution, the end-point being taken as the greatest change in potential corresponding with the addition of equal amounts of potassium permanganate solution. Ferricyanides or chlorides in moderate amount do not interfere with the estimation, but salts which yield precipitates with either ferro- or ferricyanides must not be present.²³

A method of estimating iodides by measurement of the conductivity depends on the oxidation of the iodide by means of potassium iodate solution:



The mixture is titrated with hydrochloric acid, the conductivity being measured after each addition, until a rapid increase is shown, the end-point being found by reference to the curve. The method is applicable in the presence of bromides, for the oxidation of which a higher temperature and concentration is required.²⁴

Small quantities of vanadium in steel may be estimated by dissolving the sample in nitric acid and oxidising the vanadium with nitric acid under specified conditions, which leave chromic compounds unaltered. The solution is then cooled and titrated by the electrometric method.²⁵ By a modification of the method the chromium may also be estimated.²⁶

A rapid method of estimating carbon in steel has been based on the absorption of the carbon dioxide, obtained by direct combustion, in barium hydroxide solution and measuring the change in the electrical conductivity of the solution caused by the precipitation of barium ions. The construction of a nomographic chart is described, by means of which the percentages of carbon may be read with an error of less than 0.005.²⁷

Experiments have shown that Pb^{++} may be separated from Cr^{+++} by electrolytic-precipitation as lead peroxide under certain specific conditions as to the proportions of the two metals in the solution, etc.²⁸

Chlorine, bromine, or iodine may be electrolytically estimated by an indirect method in which the halogen is precipitated as a silver salt, which is dissolved in alkaline potassium cyanide solu-

²³ G. L. Kelley and R. T. Bohn, *J. Amer. Chem. Soc.*, 1919, **41**, 1776.

²⁴ I. M. Kolthoff, *Chem. Weekblad*, 1919, **16**, 926; *A.*, ii, 370.

²⁵ G. L. Kelley, J. R. Adams, and J. A. Wiley, *J. Ind. Eng. Chem.*, 1917, **9**, 780; *A.*, 1917, ii, 512.

²⁶ G. L. Kelley, J. A. Wiley, R. T. Bohn, and W. C. Wright, *ibid.*, 1919, **11**, 632; *A.*, ii, 431.

²⁷ J. R. Cain and L. G. Maxwell, *ibid.*, 852; *A.*, ii, 476.

²⁸ J. Milbauer and J. Šetlík, *J. pr. Chem.*, 1919, [ii], **69**, 85; *A.*, ii, 372.

tion, and the latter electrolysed with a nickel-plated copper electrode and a rotating iron anode.²⁹

Water Analysis.

A rapid method of estimating the total solids in water, based on a determination of the electrical conductivity, is frequently employed, but when a mean equivalent weight and conductivity are assumed in the calculations, the results may be very erroneous in the case of different waters. It is only when the composition of the solution is known that the equivalent conductivity may be calculated, and tables for reference under such conditions have been drawn up.³⁰

For extracting and estimating dissolved gases in water, a method has been described in which a bulb, from which the air has been exhausted, is fitted to a large bottle of the water. On turning the tap below the bulb, the gases are extracted from the water, and by placing the bottle in water at about 40°, are completely removed.³¹

Attention has been directed to the fact that pure sodium carbonate is acid towards a small amount of phenolphthalein and alkaline towards a larger amount. Hence, in titrating carbon dioxide in water with sodium carbonate solution, the amount of indicator used must be proportional to the quantity of sodium carbonate. Directions are given for a method embodying this precaution.³² In order to eliminate the influence of ferrous salts which may be present, Rochelle salt may be added before titrating the water with sodium carbonate in the presence of a definite quantity of phenolphthalein.³³

The interference of chlorides in the estimation of nitrates in water by the phenolsulphonic acid method may be eliminated by using a more dilute solution of the reagent and adding it to the water prior to evaporation, which is carried out under specified conditions.³⁴

A source of error in the estimation of albuminoid ammonia in water is the presence of nitrogenous impurities in the potassium permanganate, which are only very slowly eliminated on boiling

²⁹ E. Lasala, *Anal. Fis. Quim.*, 1919, 17, 85; *A.*, ii, 239.

³⁰ I. M. Kolthoff, *Chem. Weekblad*, 1918, 15, 1160; *A.*, ii, 76.

³¹ F. W. Richardson, *J. Soc. Chem. Ind.*, 1919, 38, 32T; *A.*, ii, 167.

³² R. Czerny, *Zeitsch. anal. Chem.*, 1919, 58, 1; *A.*, ii, 297.

³³ H. Klut, *Ber. Deut. pharm. Ges.*, 1919, 29, 344; *A.*, ii, 297.

³⁴ R. C. Frederick, *Analyst*, 1919, 44, 281; *A.*, ii, 371.

the permanganate solution with alkali. This may cause the results, for albuminoid ammonia to be much too high.³⁵

A series of experiments to ascertain the velocity of absorption of chlorine by the same water in varying intervals of time has shown that the velocity constant usually increases with the time of contact. The use of colour readings as an index of chlorine absorption is only trustworthy with a given water under known conditions. The chlorine absorption does not increase in direct proportion with the increase in pollution (as indicated by the oxygen absorption), but shows decreasing acceleration. Experiments have indicated that absorption for five minutes would be as effective for the routine control of chlorination as the use of a longer time interval.³⁶

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³⁵ E. A. Cooper and J. A. Heward, *Biochem. J.*, 1919, **13**, 25; *A.*, ii, 296.

³⁶ A. Wolman and L. H. Enslow, *J. Ind. Eng. Chem.*, 1919, **11**, 209; *A.*, ii, 197.

PHYSIOLOGICAL CHEMISTRY.

BEFORE reviewing the year's work, we may record the deaths of Ivar Bang, Ludwig Brieger, Adrian Brown, Emil Fischer, and Franz Röhmnn. Bang, who died suddenly on December 11th, 1918, in the prime of life, was a Norwegian by birth, a pupil of Hammarsten, and Professor of Medical Chemistry in the University of Lund since 1904. He worked on nucleic acids, histones, and immuno-chemistry, but is best known for his micro-methods for the determination of sugar and fat in the blood. His published works include "Chemie und Biochemie der Lipide" (1911), "Der Blutzucker" (1913), "Methoden zur Mikrobestimmung einiger Blutbestandteile" (1916), and "Lehrbuch der Harnanalyse" (1918). "Die Nukleinsäuren und ihre Verbindungen" was in preparation for the series of German biochemical monographs. Brieger, known among biochemists for his work on ptomaines more than thirty years ago, was since 1900 Director of the Institute of Hydrotherapy of Berlin University. Adrian Brown was Professor of Brewing at Birmingham. To Emil Fischer biochemistry owes a debt greater than that to any other organic chemist of our generation. Röhmnn was for many years Extraordinary Professor of Physiological Chemistry at Breslau.

Among new publications, we may mention "Medical Science: Abstracts and Reviews," a monthly journal published by the Oxford University Press for the Medical Research Committee in place of the Medical Supplement to the "Review of the Foreign Press," which was issued from January, 1918, to April, 1919. "Medical Science," started in October, 1919, aims at providing a critical and selective survey of the medical publications of all countries, and should therefore be of interest to physiological chemists also. During the war, the eighth and ninth volumes of Abderhalden's "Handbuch der biochemischen Arbeitsmethoden" have appeared. The earlier volumes are now partly out of print, and a second edition is about to appear. The series "Die Biochemie in Einzeldarstellungen" was continued at the end of 1918 by No. 4, "Die Einwirkung von Mikro-organismen auf die Eiweiss-

körper" by Paul Hirsch. This very complete, if somewhat uncritical, compilation deals with acidic as well as with basic decomposition products of proteins; in particular, the physiologically active amines, like tyramine and histamine, are fully dealt with. The third monograph of this series, "Über künstliche Ernährung und Vitamine," by F. Röhmman, was noticed two years ago.¹ A most valuable "Report on the present state of knowledge concerning accessory food factors (vitamines)" has appeared in the special report series of the Medical Research Committee. It is by a committee consisting of F. G. Hopkins (chairman), H. Chick, J. C. Drummond, A. Harden, and E. Mellanby. Second editions of W. M. Bayliss's "General Physiology" and of H. Bechhold's "Die Kolloide in Biologie und Medizin" have appeared. "The Nature of Enzyme Actions," by the former author, has reached its fourth edition, and "Practical Physiological Chemistry," by S. W. Cole, its fifth. The latter book was originally written for students only, but has now been so much revised and enlarged by the addition of well-chosen recent methods that it will be found useful in research laboratories.

Reviewing the year's work as a whole, we must recognise that, at least as regards publications, we are still in a period of transition. Probably nearly all war problems have been abandoned by now, but in the matter of publication there is a hysteresis. For instance, it is only during the present year that the fermentation process of manufacturing glycerol from sugar has come to light. As one of its effects on biological chemistry, the war has left an increased interest in food problems, especially those concerned with accessory food substances and deficiency diseases.

The Radioactivity, and Biological Importance of Potassium.

The fact that of the dozen or fifteen elements essential to life, potassium² is the only one which possesses a distinct, if minute, radioactivity, induced H. Zwaardemaker³ to replace it in Ringer's solution by other radioactive elements. Ringer discovered long ago that, in order to keep the isolated frog's heart beating normally for a prolonged period, the perfusion fluid must contain potassium as well as calcium and sodium salts; he also showed that the potassium may be replaced by an equivalent amount of rubidium or of caesium, but if these salts were entirely omitted, the heart

¹ *Ann. Report*, 1917, 184.

² See *ibid.*, 1909, 266 for references.

³ For a résumé of Zwaardemaker's researches and those of his pupils, see *Pflüger's Archiv*, 1918, 173, 28.

soon stops beating. Now rubidium⁴ also has a distinctive β -activity far less penetrating than that of potassium. The β -radiation of caesium of very low penetrating power seems to be absorbed so readily as to escape detection altogether, but it is postulated by Zwaardemaker on biological grounds.⁵ As a preliminary, he and T. P. Feenstra,⁶ calculated the amount of other elements radioactively equivalent to the potassium in Ringer's solution.

Zwaardemaker and his pupils showed that the frog's heart continues to beat equally well if a litre of the perfusion fluid contains, instead of 100 mg. of potassium chloride, 25 mg. of uranyl nitrate, 50 mg. of thorium nitrate, and 0.000005 mg. of radium bromide, or a minute quantity of niton (about 100 Mache units). This means that a heart which has stopped beating owing to perfusion with potassium-free Ringer's solution begins to beat again when an equi-radioactive amount of another element is added to the perfusion fluid. Moreover, a heart may be made to resume pulsation by exposure to β -radiation from mesothorium or from radium at a distance of 1—2 cm.⁷

The amounts of radioactive elements quoted above refer to frogs in winter; in summer, smaller amounts suffice, and a reduction in the necessary amount may also be brought about by adding fluorescein or eosin to the perfusion fluid; in either case, the reduction seems to be due to improved adsorption of the radioactive element by the endothelium. The adsorption of electrically charged particles seems also to be the explanation of the following paradox. The various means of keeping a heart pulsating, or restoring its beat when it has stopped, may be arranged in two groups, namely,

potassium	}	{	uranium
rubidium			thorium
caesium			radium
β -radiation			niton

A heart beating under the influence of any one agent will continue to do so if we switch over to a perfusion fluid containing the appropriate amount of another member of the same group, but is at once stopped by a member of the other group. Thus, rubidium-Ringer's solution or β -radiation will re-start a heart stopped by a Ringer's solution free from a radioactive element, and such a heart will continue to beat if we switch over to caesium—

⁴ N. Campbell, *Proc. Camb. Phil. Soc.*, 1909, 15, 11; *A.*, 1909, ii, 288.

⁵ *Proc. K. Akad. Wetensch. Amsterdam*, 1917, 20, 773.

⁶ *Ibid.*, 1916, 19, 99, 341, 633; *A.*, 1917, i, 70, 105, 241.

⁷ H. Zwaardemaker and J. W. Lely, *Arch. Néerland. Physiol.*, 1917, 1, 745.

Ringer's solution, for instance, but will stop if we next perfuse it with a solution containing uranium or any other member of the second group. Conversely, a heart beating under the influence of a solution containing radium is stopped by ordinary Ringer's solution containing potassium. In order to change over⁷ from one group to the other, it is necessary first to wash out the heart with a solution free from radioactive elements; accordingly, a mixture from both groups stops pulsation. Zwaardemaker finds the explanation of these paradoxical results in the fact that in the first group we are concerned with negatively charged β -radiation, in the second with positively charged α -particles. (In the case of radium, which sends out both kinds, α -particles predominate.) The adsorption of either kind of particle gives the heart the electric charge which appears to be necessary, but in a mixture of both kinds the particles with opposite charge neutralise each other, so that the requisite electrical condition of the heart does not result. The radioactive "equilibrium," due to electrical neutralisation, between potassium and uranium is different in summer and in winter, and is also modified by fluorescein,⁸ because the adsorption of these two elements is affected unequally (see above). Zwaardemaker⁹ has furnished a most interesting botanical analogy to the above-mentioned antagonism between α - and β -radiation. The centres of plate cultures of luminous bacteria were exposed to β -radiation from mesothorium and to α -radiation from polonium, and the cultures were subsequently photographed by their own light, when in both cases the centre was found to be black, on account of the local death of the organism as a result of radiation. When, however, part of the mesothorium field was simultaneously exposed to polonium radiation, colonies developed in this area, where the two kinds of radiation apparently neutralised each other. This is an example of the antagonism, it should be noted, between two radiations, whereas in the experiments on the frog's heart at least one side of the antithesis is concerned with ordinary matter.

These experiments with minute unicellular organisms are further of considerable interest in showing that both kinds of radiation affect the protoplasm of one and the same cell; obviously we are here concerned with a general phenomenon, and it is not surprising that other examples have been found, relating to vagus inhibition,¹⁰ skeletal muscle, endothelium of the blood vessels, and to the permeability of the kidney epithelium. H. J. Hamburger and

⁸ H. Zwaardemaker, *Proc. K. Akad. Wetensch. Amsterdam*, 1918, 20, 768; A., 1918, ii, 182.

⁹ *Ned. Tijdschr. v. Geneesk.*, 1919, i, 250.

¹⁰ H. Zwaardemaker and J. W. Lely, *Arch. Néerland. Physiol.*, 1917, 1, 745.

R. Brihman¹¹ showed that when the frog's kidney is perfused from the abdominal aorta with a solution free from potassium, the kidney becomes abnormally permeable to dextrose. At Zwaardemaker's suggestion, these authors replaced the potassium chloride by a small quantity of uranyl nitrate, and found this equally active in restraining the dextrose from passing the kidney, but a mixture of potassium and uranium was found to be inactive, in accordance with what was said above.

Inorganic.

E. Winterstein¹² has detected iodine in the beetroot, potato, celery, lettuce, and carrot, but failed to find it in thirty-six other plants; he also failed to find it in milk, cheese, and cow's urine. The method allows of the detection of 0.04 mg. of iodine added to 10 grams of spinach. The presence of selenium in animals, especially in bones and teeth, and in plants has been asserted by T. Gassmann,¹³ but R. Fritsch¹⁴ has lately failed to confirm this observation, especially as regards plants; his method allows of the detection of 0.5—2 mg. in 30—50 grams of plant material. Zinc has been found to be constantly present in animal cells, and occurs more particularly in the venom of serpents, to the extent of 0.11—0.56 per cent.¹⁵ It is here combined with organic constituents (perhaps a proteose rich in sulphur), so that it cannot be precipitated by hydrogen sulphide, nor does it dialyse. The zinc contents of venoms are in inverse order of their proteolytic and coagulating powers, but in the same order as their nucleolytic and diastatic activities. Traces of zinc have also been found in various foods.¹⁶ Thus hen's eggs contain about 1 mg., nearly all in the yolk; cow's milk contains, on an average, 4.2 mg. per kilo., human milk distinctly more. The same metal is invariably present in oysters grown in Atlantic waters; the amount could not be correlated with that of the water in which the oysters grew. Probably copper is always present also.¹⁷

Proteins.

The work of various investigators has made it probable that euglobulin and pseudoglobulin of serum are very closely related.

¹¹ *Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 944.

¹² *Zeitsch. physiol. Chem.*, 1918, **104**, 54; *A.*, i, 190.

¹³ *Ibid.*, 1916, **97**, 307; 1917, **100**, 182; *A.*, 1916, i, 772; 1917, ii, 540.

¹⁴ *Ibid.*, 1918, **104**, 59; *A.*, i, 191.

¹⁵ C. Delezenne, *Ann. Inst. Pasteur*, 1919, **33**, 68; *A.*, 1917, i, 187.

¹⁶ V. Birckner, *J. Biol. Chem.*, 1919, **38**, 191; *A.*, i, 420.

¹⁷ R. S. Hiltner and H. J. Wichmann, *ibid.*, 205; *A.*, i, 421.

Thus H. Chick¹⁸ described an artificial euglobulin which she regarded as a mechanical complex originating from the mutual precipitation of pseudoglobulin and a lipid substance. P. Hartley¹⁹ could find no difference on analysis of the two proteins by Van Slyke's method, and, using the same method, C. Crowther and H. Raistrick²⁰ failed to find any difference between the euglobulin and pseudoglobulin of cow's colostrum and between these proteins and the corresponding ones in ox serum. H. W. Dudley and H. E. Woodman²¹ have examined the colostrum globulins by the racemisation method of Dakin and Dudley.²² The optical properties of the amino-acids obtained after racemisation and hydrolysis, as well as the rate at which racemisation proceeds, are identical in agreement with the supposed identity of the two globulins of colostrum. A comparative study of the caseinogens of the cow and sheep, however, by H. W. Dudley and H. E. Woodman,²³ who used the delicate method of Dakin and Dudley, referred to above, revealed at least a difference in the "make up" of these caseinogens from closely related species; their constituent amino-acids are arranged differently. Now H. D. Dakin and H. H. Dale²⁴ have supplied a second example of structural difference in the corresponding proteins of allied species, and have added additional interest to the result by showing that the two proteins are also antigenically different, thus suggesting a chemical basis for at least some case of antigenic specificity. They chose the crystalline egg-albumins of the hen and the duck. After partial racemisation by $N/2$ -alkali at 37° and subsequent hydrolysis by sulphuric acid, definite differences were found in the optical properties of the leucine, the aspartic acid, and the histidine. The quantities of these and of the other amino-acids obtained were very similar in the two cases, so that the difference between hen's and duck's albumin seems to be a difference in the arrangement of the same constituent amino-acids. This difference is, however, sufficient to give an antigenic specificity, for the two crystalline proteins behave as distinct antigens for the anaphylactic reaction. Most of the experiments were made by sensitising virgin guinea-pigs to one protein and examining successively the effects of both proteins on the surviving isolated uterus. In order to give an idea of the extreme delicacy of this reaction, it may be noted that in one case

¹⁸ *Biochem. J.*, 1914, 8, 404; *A.*, 1914, i, 1145.

¹⁹ *Ibid.*, 541; *A.*, 1914, i, 1206. ²⁰ *Ibid.*, 1916, 10, 434; *A.*, 1916, i, 864.

²¹ *Ibid.*, 1918, 12, 339; *A.*, i, 178.

²² *J. Biol. Chem.*, 1913, 15, 263, 271; *A.*, 1913, i, 1249; *Ann. Report*, 1913, 192.

²³ *Biochem. J.*, 1915, 9, 97; *A.*, 1915, i, 468.

²⁴ *Ibid.*, 1919, 13, 248.

0.0001 mg. of albumin in a bath containing 50 c.c. of Ringer's solution produced a very distinct contraction of the sensitised uterus, that is, a concentration of the specific antigen of 1:500,000,000.

Amino-acids.

The introduction of Emil Fischer's method of separating mono-amino-acids by the fractional distillation of their esters led to numerous investigations on the amino-acid content of various proteins. Naturally, these investigations were of very unequal value. After the first decade, when the technique had been thoroughly worked out, we find investigators carefully considering the sources of loss involved in the process, for even in the most favourable cases the amino-acids isolated do not represent even approximately the whole of the protein hydrolysed. The experimental losses affect almost entirely the monamino-acids, and are difficult to overcome. In the case of zein, the amino-acids isolated amounted to 85 per cent., but this includes the water taken up in hydrolysis; the results of this investigation led Osborne to a careful consideration of the sources of loss. Apart from experimental errors, one of these sources might be the presence of unknown cleavage products which had entirely escaped detection. Subsequently, norleucine, and probably also α -aminobutyric acid,²⁵ were recognised as possible constituents of protein, but during the second decade, after the introduction of the ester method, there has been a great falling off in its application, and interest has shifted to D. D. Van Slyke's methods²⁶ for finding the distribution of nitrogen in various groups, according to its mode of combination, without isolating individual amino-acids.

It is all the more interesting, therefore, that H. D. Dakin²⁷ has found a new method for separating amino-acids which promises to be of great use, and has already revealed the presence in casein of a new cleavage product in an amount of more than 10 per cent. As is so often the case, progress depended on the introduction of a new technique. Dakin found that, contrary to expectation, certain amino-acids can be extracted from aqueous solution by partly miscible solvents, in particular by butyl alcohol, which is now available as a by-product in the fermentation process of acetone manufacture. He hydrolyses the protein with sulphuric acid, removes the latter quantitatively with barium hydroxide, concentrates, and allows the tyrosine to crystallise out. The filtrate from the tyrosine is further concentrated, made approximately

²⁵ *Ann. Reports*, 1913, 198.

²⁶ *Ibid.*, 1911, 179.

²⁷ *Biochem. J.*, 1918, 12, 290; *A.*, i, 150.

neutral to litmus, and then extracted in a continuous apparatus with butyl alcohol, preferably at 60–80°. Of course, the process is not very rapid, but the surprising thing is that any amino-acids should be extracted at all. The coefficient of partition is entirely in favour of the aqueous solution, but soon after the extraction has been started amino-acids begin to crystallise from the butyl alcohol in the boiling flask. With reference to this “apparent paradox,” Dakin observes that the presence of water is a conditioning factor, and that the passage of a certain proportion of water from the fluid undergoing extraction to the butyl alcohol medium is essential. An excess of a salt, such as calcium chloride, in the aqueous phase almost entirely prevents the extraction of amino-acids. I refer to these practical details because I feel, with Dakin, that the use of butyl alcohol and similar solvents will be found of value for many other purposes in biochemistry.

Now as regards the kind of amino-acids extracted, it is found that proline comes out most readily, as was to be expected, since this is the only amino-acid appreciably soluble in ethyl alcohol. Dakin obtains the proline in a fairly pure solution without racemisation in a yield corresponding with 8 per cent. of the caseinogen hydrolysed. D. D. Van Slyke²⁸ found that 7.13 per cent. of the nitrogen in caseinogen is in the non-amino-form, corresponding with 9.2 per cent. of free proline (if we exclude hydroxyproline). Yet Abderhalden by the ester method could only isolate 3.1 per cent. of proline, and that partly racemised.

In addition to proline, butyl alcohol extracts all the mono-basic monoamino-acids (alanine, valine, leucine, etc.), and this mixture is at once obtained in a form suitable for separation by the ester method. Tryptophan is also extracted by butyl alcohol from a solution after one precipitation by Hopkins' reagent.

The more strongly ionised diamino-acids and the dicarboxylic monoamino-acids are not extracted under the conditions described by Dakin. The former may be precipitated by phosphotungstic acid, leaving the latter (aspartic and glutamic acids) in a relatively pure state. It was owing to this that Dakin could obtain 21 per cent. of the caseinogen as glutamic acid hydrochloride, again much more than the yield previously obtained by the ester method, and the yield of aspartic acid (as crystalline copper salt) was two or three times as large as that previously recorded, but the chief loss occurring in this fraction in the older method is due to a new dibasic aminohydroxy-acid, of which Dakin isolated 10.5 grams from 100 grams of caseinogen.

This new acid is almost certainly α -amino- β -hydroxyglutaric or

²⁸ *J. Biol. Chem.*, 1911, 9, 205; *A.*, 1911, ii, 780.

β -hydroxyglutamic acid, $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. For the evidence for its constitution, Dakin's paper should be consulted.

It is probable that β -hydroxyglutamic acid had already been partly separated by F. W. Foreman,²⁹ who was unable to pursue his investigations. The reason why such a relatively abundant constituent should have escaped the notice of the numerous investigators of caseinogen would appear to be that the free acid is extremely readily soluble in water and crystallises only slowly from its syrupy solution. The diethyl ester does not distil without decomposition, and, on heating, the acid is rapidly converted into hydroxypyrrolidonecarboxylic acid. It seems conceivable that hydroxyglutamic acid is the precursor of the base carnitine (novaine) occurring in meat extract.

The Origin of Alkaloids from Amino-acids.

After the chief amino-acids of protein had become known, various chemists, who saw in them the precursors of the vegetable alkaloids, began to speculate on the manner in which the alkaloids might be derived from the amino-acids. The first serious speculation of this kind is due to A. Pictet,³⁰ who laid great stress on the methylation of hydroxy- and imino-groups by means of formaldehyde. He naturally regarded alkaloids containing a pyrrole or indole ring as resulting from proline, hydroxyproline, and tryptophan, but he also derived from the same source piperidine, pyridine, and quinoline rings, which do not occur in protein. He imagined that methylated pyrroles and indoles undergo isomeric change to their ring homologues pyridine and quinoline, because 1-methylpyrrole when distilled through a red-hot tube, yields a small quantity of pyridine.³¹ The next extensive speculation on the phytochemical synthesis of alkaloids was by E. Winterstein and G. Trier,³² who adopted some of Pictet's ideas, but did not consider the latter's pyridine synthesis sufficiently biochemical, and instead derived pyridine from lysine, which Drechsel had already considered as a possible parent substance of alkaloids, when he discovered it as the first basic degradation product of protein. The latest and most elaborate paper on this subject is due to R. Robinson³³; theoretically it marks a

²⁹ *Biochem. J.*, 1914, 8, 463; *A.*, 1914, ii, 826.

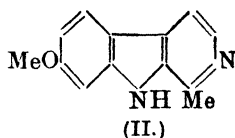
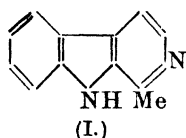
³⁰ *Arch. Sci. phys. nat.*, 1905, [iv], 19, 329; *Arch. Pharm.*, 1906, 244, 389; *A.*, 1905, i, 541. See also F. Czapek, "Biochemie der Pflanzen," vol. II, p. 267. A. Windaus and F. Knoop, *Ber.*, 1905, 38, 1166; *A.*, 1905, i, 381.

³¹ *Ber.*, 1904, 37, 2792; *A.*, 1904, i, 771.

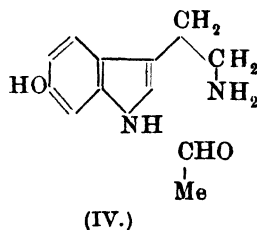
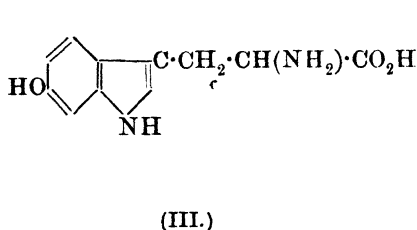
³² "Die Alkaloide," 1910, pp. 263-317.

³³ *Ann. Report*, 1917, 135.

great advance, owing to the simplicity of the reactions postulated. From another point of view, however, such speculations may be regarded as mere *jeux d'esprit*. The chief value of a theory is in the experiments which it suggests, and, judged by this test, Robinson's theory is seen to be of outstanding importance³⁴ and on a different plane from the speculations of his predecessors. Not only did it suggest to him a simple new synthesis of tropinone,³⁴ which Willstätter had already regarded as the precursor of atropine and of cocaine in plants, but it has now led to the elucidation of the constitution of the alkaloids harmine and harmaline,³⁵ and, at the same time, of the mysterious base, $C_{12}H_{10}N_2$, obtained by F. G. Hopkins and S. W. Cole³⁶ in the oxidation of tryptophan, for the latter base is identical with harman, a derivative of both alkaloids. Harman, moreover, occurs in nature, for recently E. Späth³⁷ has shown that it is identical with the alkaloid aribine from *Arariba rubra*, Mart; the old formula, $C_{23}H_{20}N_4$, previously assigned to this alkaloid is erroneous. Harman, aribine, and the oxidation product of tryptophan all have almost certainly the constitution I.



Harmine would then have the constitution II, and harmaline two additional hydrogen atoms in the pyridine ring. Perkin and Robinson discuss the synthesis of the two alkaloids in the plant. They consider that the starting point is a hydroxytryptophan (III),



which is decarboxylated and condensed with aldehyde (IV), probably derived from alanine. The condensation product would be methylated to harmaline by formaldehyde on the lines suggested by Pictet (above), and the harmaline oxidised to harmine. Perkin and Robinson are sufficiently bold to predict that this

³⁴ *Ann. Report*, 1917, 134.

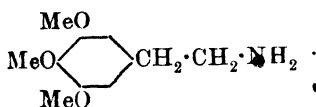
³⁵ W. H. Perkin, jun., and R. Robinson, *T.*, 1919, 115, 967.

³⁶ *J. Physiol.*, 1903, 29, 451; *A.*, 1903, i, 590.

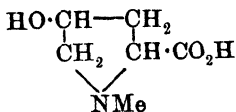
³⁷ *Chem. Zeit.*, 1919, 43, 555.

hydroxytryptophan will be found among the amino-acids from vegetable proteins. E. Abderhalden and L. Baumann³⁸ have, indeed, stated that a hydroxytryptophan accompanies tryptophan, but beyond a few analyses nothing further has been published about this substance. Perhaps it would be more hopeful to search for it in plants; thus, a hydroxytyrosine (3:4-dihydroxyphenyl-alanine) has been isolated from *Vicia faba* by M. Guggenheim,³⁹ although it has never been obtained from protein. Perkin and Robinson also discuss how the base $C_{12}H_{10}N_2$ (=harman=aribine) might arise from tryptophan, $C_{11}H_{12}O_2N_2$. As the amino-acid has been decarboxylated, not one, but two carbon atoms must have been added, which might come from accompanying alanine or from alcohol or other impurity in the reagents employed, or even from another molecule of tryptophan. The experimental conditions for obtaining the base are not well understood. Professor Hopkins informs me that on several occasions a yield of 30 per cent. was obtained, on other occasions nothing. It is furnished by pure tryptophan, so that alanine probably plays no part in its formation. A. Ellinger⁴⁰ failed to isolate it in numerous experiments; the mechanism of its formation remains a mystery.

Other plant alkaloids which are obviously derived from amino-acids are tetramethylputrescine, from arginine via ornithine, and hordenine from tyrosine. Hordenine has acquired additional interest, since E. Späth⁴¹ has shown it to be identical with anhaline, an alkaloid from Mezcal buttons (*Cactaceae*). The chief alkaloid, mezcaline, which has a peculiar physiological action, is found by Späth to have the somewhat similar constitution:



An *N*-methylhydroxyproline (4-hydroxyhygric acid) has been discovered in the bark of *Croton gubouga*, S. Moore.⁴² This substance has two optically active carbon atoms, and probably the same con-



³⁸ *Zeitsch. physiol. Chem.*, 1908, 55, 412; *A.*, 1908, i, 488.

³⁹ *Ibid.*, 1913, 88, 276; *A.*, 1914, i, 49.

⁴⁰ *Ber.*, 1906, 39, 2515; *A.*, 1906, i, 696.

⁴¹ *Monatsh.*, 1919, 40, 129; *A.*, i, 548.

⁴² J. A. Goodson and H. W. B. Clewer, *T.*, 1919, 115, 923.

figuration as *l*-hydroxyproline from proteins. On methylation, it yielded a mixture of the two stereoisomeric betaines, betonidine and turidine, from *Betonica officinalis*.⁴³ According to H. Leuchs and K. Bormann,⁴⁴ turidine is very likely formed from betonidine by racemisation (of the α -carbon atom only) during extraction and during the methylation of *l*-hydroxyproline.

Histamine.

Histamine (β -iminazolyethylamine) continues to attract attention on account of its powerful physiological action and Pyman's synthesis has been repeated and elaborated.⁴⁵ There are so many successive reactions involved that the yield of histamine is only 4.2 per cent. of that theoretically possible from the citric acid employed. It would seem preferable, therefore, to prepare cyanomethylglyoxaline from histidine by Dakin's method⁴⁶ (yield, 80 per cent.), and reduce this nitrile to histamine, thus eliminating all stages but the last of Pyman's synthesis.

The investigation of the physiological action of histamine has been continued, and it has been shown that the shock-like condition which is brought about in cats by injection of 1 mg. and upwards per kilo. depends on an action on the capillary endothelium, of such a nature that a large part of the blood collects in dilated capillaries, whilst part of the plasma escapes from the vessels into the tissues.⁴⁷ The significance of histamine in surgical shock is doubtful, and the same may be said of anaphylactic shock, where the similarity of symptoms to histamine poisoning is the only reason for postulating its presence. It is still a question whether histamine is only a product of bacteria and fungi or whether it is also formed by the tissues of the higher animals. Dale and I found it, indeed, in small quantity in the intestinal mucous membrane of the ox,⁴⁸ but it seemed likely that its presence could be explained by the action of intestinal bacteria. Recently, however, J. J. Abel and S. Kubota⁴⁹ have concluded that histamine is "a widely distributed constituent of animal tissues, organ extracts, and enzymatic pro-

⁴³ A. K ng and G. Trier, *Zeitsch. physiol. Chem.*, 1913, **85**, 209; *A.*, 1913, i, 708.

⁴⁴ *Ber.*, 1919, **52**, [B], 2089; *A.*, 1920, i, 85.

⁴⁵ K. K. Koessler and M. T. Hanke, *J. Amer. Chem. Soc.*, 1918, **40**, 1706; *A.*, i, 4.

⁴⁶ *Biochem. J.*, 1916, **10**, 319; *A.*, 1916, i, 598.

⁴⁷ H. H. Dale, P. P. Laidlaw, and A. N. Richards, *J. Physiol.*, 1919, **52**, 110, 355.

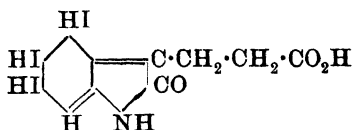
⁴⁸ G. Barger and H. H. Dale, *ibid.*, 1911, **41**, 499; *A.*, 1911, ii, 217.

⁴⁹ *J. Pharm. Expt. Ther.*, 1919, **13**, 243; *A.*, i, 506.

ducts, such as Witte's peptone," and that its occurrence here is "entirely independent of micro-organisms." They also state that it is formed early in the hydrolysis of pure proteins, and that it is identical with that constituent of the posterior lobe of the pituitary body which stimulates plain muscle. These results, if confirmed, will have great physiological significance. Abel and Kubota isolated histamine from the intestinal mucosa of the dog by a process which left no chance for post-mortem changes. From other organs, such as dog's liver and striated muscle, boiled immediately after death, they did not actually isolate histamine, but they extracted by a similar chemical procedure a substance having a closely similar pharmacological action. It is, however, their identification of histamine with a pituitary active principle which will arouse most interest. There is no doubt that they isolated histamine dipicrate in small quantity from commercial, dry, entire pituitary gland, but the exact significance to be attached to this finding is not yet quite clear. Whether histamine occurs as such in the posterior lobe of the fresh gland or whether it is formed by autolysis during drying is doubtful, and in any case there is a good deal of evidence, both chemical and pharmacological, which prevents the identification of histamine with the specific plain muscle stimulant, contained in the posterior lobe. Incidentally, it should be noted that the claim of the Farbwerke vorm. Meister, Lucius & Brüning⁵⁰ to have isolated the active principles in a crystalline form is unfounded. According to J. J. Abel and M. C. Pincoffs,⁵¹ the "hypophysin" of the Hoechst works is a mixture of albumoses with varying and unknown amounts of active and inactive constituents.

Hormones.

A pituitary hormone has been discussed in the previous section. E. C. Kendall⁵² has now published a full paper on the isolation of thyroxin, the thyroid hormone, but this communication is a consolidation of previous publications, rather than an extension thereof; the formula:



given in last year's Report⁵³ is retained, but no indication is as yet

⁵⁰ D.R.-P. 268841; A., 1914, i, 756. Compare H. Fühner, *Zeitsch. f. d. ges. exp. Medizin.*, 1913, 1, 397.

⁵¹ *Proc. Nat. Acad. Sci.*, 1917, 3, 507.

⁵² *J. Biol. Chem.*, 1919, 39, 125; A., i, 496.

⁵³ *Ann. Report*, 1918, 170.

given of the manner in which it was arrived at. The synthesis by Osterberg, first carried out in 1917, has been repeated in 1919, but no hint is given as to the method employed. The isolation of the natural substance is, however, fully described and illustrated, and it is stated that some three tons of fresh thyroid glands, chiefly pigs', have been used in the research, which has been in progress since 1910. Thyroxin may exist in three forms, a ketonic or lactam form, as represented above, a tautomeric enolic or lactim form, and a hydrated form, in which the ring is opened. This opening of the pyrrole ring seems also to occur on acetylation, for the *N*-acetyl derivative yields a disilver salt. Perhaps the method of publication is not unconnected with a desire to protect the synthesis by patent. Organic and biological chemists will await with the greatest interest the evidence for the constitutional formula and the method of synthesis, particularly with regard to the position of the three iodine atoms. Even the elementary analysis must present considerable difficulty, for the above compound contains about 67 per cent. of iodine and only 1.60 per cent. of hydrogen. If it were not hydrated in the benzene ring and contained two hydrogen atoms less, this would only lower its hydrogen content by 0.35 per cent. Kendall has also published further observations on the remarkable physiological action of thyroxin.⁵⁴ A dose of 1 milligram increased the metabolic rate of an adult by 2 per cent, but when the imino-hydrogen is displaced the substance becomes inactive. Both thyroxin and *N*-substituted derivatives accelerate the metamorphosis of the tadpole. This acceleration is also brought about by other iodine compounds and by iodine itself, and is therefore not nearly as specific as the great effect on metabolism. It was shown previously that thyroxin produces in minute doses all the therapeutic effects of the entire gland in cretinism and in myxœdema.

A hormone of a different type, non-specific and less active, has been isolated by J. W. Le Heux⁵⁵ in Magnus's laboratory. It had been shown previously⁵⁶ that washed portions of the alimentary canal (of rabbits, dogs, and cats), suspended in water or Tyrode solution, give off a substance capable of stimulating the surviving small intestine to increased movement. Le Heux has shown this substance to be choline. The surviving small intestine of a rabbit may give off 1—3 mg. per hour. The base was not identified until it was found by chance that the use of glacial acetic acid in an

⁵⁴ *Proc. Amer. Physiol. Soc., Amer. J. Physiol.*, 1919, **49**, 136.

⁵⁵ *Pflüger's Archiv*, 1919, **173**, 8. Compare *Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 805; *A.*, 1918, **i**, 323.

⁵⁶ W. Weiland, *ibid.*, 1912, **147**, 171.

attempted purification greatly increased its activity, owing to acetylation. Acetylcholine is about 400—2500 times as active as choline in stimulating the movements of the rabbits' intestine. It was also known that the acetyl derivative is very much more potent than choline itself in lowering blood pressure; acetylation here increases the activity 5000—10,000 fold, and the same ratio applies to its action on the isolated frog's heart. Le Heux finally isolated the minute quantity of choline given off from the rabbit's intestine as crystalline platini- and auri-chlorides, and considers that choline is a natural hormone and the chief cause of the automatic movements of the intestine.

Glycerol and some of its Derivatives.

The industrial production of glycerol by the action of yeast on dextrose is referred to in a subsequent section on fermentation. This process was a direct result of the war shortage of glycerol; the same cause led to experiments on the utilisation of fatty acids as food by a committee of the Royal Society,⁵⁷ who have confirmed older experiments that such acids can be utilised by the organism to a very high extent. They show that this applies also to fatty acids from "hardened" oils, for example, whale oil. Vitamines are, however, completely destroyed in the process of hardening. As the fatty acids are somewhat unpalatable, feeding experiments have been made before with their ethyl esters, which are also very well utilised. A closer approximation to the natural fats has been obtained by A. Lapworth and Mrs. L. K. Pearson,⁵⁸ who distilled olive oil and stearin with mannitol and 1.5—2 per cent. of dry sodium ethoxide. Glycerol passes over in a yield of nearly 80 per cent., and the residue in the flask consists of a complex mixture of oleates or stearates (of mannitol, mannitan,⁵⁹ and isomannide?). According to W. D. Halliburton, J. C. Drummond, and R. K. Cannan,⁵⁹ the "mannitol" olive oil is utilised by the animal organism to practically the same extent as olive oil itself. As these authors remark, the importance that was attached to the investigation during the war is fortunately now no longer so great.

With a view to studying the action of lipolytic ferments, E. Abderhalden and E. Eichwald,⁶⁰ some five years ago, prepared a number of optically active fats from optically active epibromohydrins, but the specific rotation of the fats was very small. With

⁵⁷ *J. Physiol.*, 1919, **52**, 328.

⁵⁸ *Biochem. J.*, 1919, **13**, 296; *A.*, i, 570.

⁵⁹ *Id.*, 301.

⁶⁰ *Ber.*, 1914, **47**, 1856; *A.*, 1914, i, 801.

the same end in view, these authors have more recently prepared optically active propylene glycol⁶¹ by the resolution of β -chloro-*n*-propylamine which was converted successively into optically active β -chloro- α -propanol, propylene oxide, propylene glycol, and its dibutyrin. Incidentally, this work led to the synthesis of the optically active, biologically important *l*-hydroxybutyric acid, which was prepared from *d*-propylene oxide, and is found to have the same configuration as *l*-alanine. The same authors,⁶² by treating *d*- α -bromohydrin, previously prepared, by them, in dry pyridine solution with phosphoryl chloride, have also obtained optically active glycerophosphoric acid, which must be the first step in the synthesis of a phosphatide, since natural glycerophosphoric acid is optically active.

A curious biochemical degradation of glycerol has been discovered by E. Voisenet,⁶³ who has described a new organism in bitter wines, *Bacillus amaracrylus*, which has the characteristic reaction of dehydrating glycerol to acraldehyde.

Some Tissue Constituents.

Cholesterol and the bile acids are the only representatives in the animal organism of polycyclic hydroaromatic compounds; both cholesterol and cholic acid have four reduced rings, and a relationship between these substances has been suspected for a long time, all the more because cholic acid and some of its derivatives give colour reactions similar to those of cholesterol. Thus, H. Wieland and F. J. Weil⁶⁴ showed that cholatrienecarboxylic acid, formed by the distillation of cholic acid under diminished pressure, gives the Liebermann-Burchard cholesterol reaction, and I. Lifschütz⁶⁵ concluded that cholic acid is derived from cholesterol on account of a remarkable colour reaction, given in identical manner by both substances. A definite proof of the relationship has, however, only been furnished recently.⁶⁶ The difference in the number of carbon atoms of cholesterol (27) and of cholic acid (24) is due to the presence of an additional *isopropyl* group in the former compound; on oxidation with chromium trioxide, these three carbon atoms are removed as acetone, which cholic acid does not yield under these conditions. Owing to the further presence of an alcoholic hydroxyl group and of a double bond, it is impossible to remove the *isopropyl*

⁶¹ *Ber.*, 1918, **51**, 1312; *A.*, i, 2.

⁶² *Ibid.*, 1308; *A.*, i, 3.

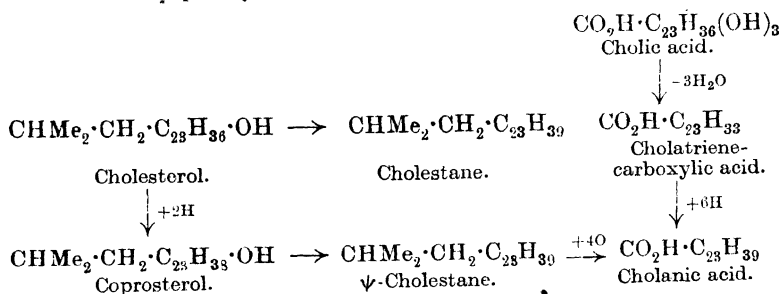
⁶³ *Ann. Inst. Pasteur*, 1918, **32**, 476; *A.*, i, 55.

⁶⁴ *Zeitsch. physiol. Chem.*, 1912, **80**, 287; *A.*, 1912, i, 830.

⁶⁵ *Ber.*, 1914, **47**, 1459; *A.*, 1914, i, 657.

⁶⁶ A. Windaus and K. Neukirchen, *ibid.*, 1919, **52**, [B], 1915; *A.*, 1920, i, 41.

group from cholesterol itself without destroying the rest of the molecule. The displacement of the hydroxyl by hydrogen and the reduction of the double bond furnishes cholestane, $C_{27}H_{48}$, and when this hydrocarbon is oxidised with chromium trioxide, there results the acid, $C_{24}H_{40}O_2$, which is isomeric with cholanic (cholanecarboxylic) acid, a reduction product of the cholatrienecarboxylic acid, $C_{24}H_{34}O_2$, of Wieland and Weil, referred to above. The acids, $C_{24}H_{40}O_2$, from cholesterol and from cholic acid are, indeed, very similar; they are not identical, however. Their close similarity reminded Windaus and Neukirchen of that existing between dihydrocholesterol obtained from cholesterol by ordinary chemical reduction and coprosterol, its reduction product formed by intestinal bacteria. The latter alcohol is derived, not from cholestane, but from a diastereomeric hydrocarbon, ψ -cholestane (coprostan).⁶⁷ Now the cholanic acid of Wieland and Weil is derived from ψ -cholestane. On oxidation, the latter hydrocarbon yields acetone and an acid, $C_{24}H_{40}O_2$, isomeric with that from cholestane and identical with the reduction product of cholatrienecarboxylic acid. Hence this is the bridge between cholesterol and the bile acids. The relationship may be summarised as follows:



It is noteworthy that the two naturally occurring derivatives of cholesterol, namely, coprosterol and cholic acid, are both derived from ψ -cholestane, and not from cholestane, the laboratory reduction product of cholesterol.

The chemistry of the lipoids is being simplified by Levene and his collaborators, and there are indications that the number of individuals in this group is smaller than has been supposed. Thus, cuorin, the name given to the lecithin-like substance from heart and other muscles,⁶⁸ is, according to P. A. Levene and S. Komatsu,⁶⁹ not an individual, but an impure kephalin, in agreement with the

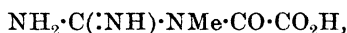
⁶⁷ Compare A. Windaus and C. Uibrig, *Ber.*, 1915, 48, 857; *A.*, 1915, i, 678.

⁶⁸ A. Erlandsen, *Zeitsch. physiol. Chem.*, 1907, 51, 71; *A.*, 1907, i, 371.

⁶⁹ *J. Biol. Chem.*, 1919, 39, 83, 91; *A.*, i, 466.

view already expressed by H. Maclean.⁷⁰ The so-called lecithin from heart muscle is a mixture of lecithin and kephalin; on reduction with hydrogen and palladium, the substance has all the properties of crude hydrolecithin of egg-yolk,⁷¹ and can be fractionated into hydrolecithin and hydrokephalin. According to Levene and Komatsu, the opinion of Fränkel and Linnert,⁷² that there are specific phosphatides in the individual organs of the same animal, is unfounded. Perhaps the number may be reduced to two, namely, lecithin and kephalin. As usually prepared, kephalin is mixed with its decomposition products, chiefly arising through loss of a fatty acid group, either by enzymes or by chemical manipulation.

The existence of methylguanidine in normal urine had already been rendered very doubtful by A. J. Ewins,⁷³ who suggested that it is formed by oxidation from creatinine during the precipitation with silver salts in alkaline solution. T. Greenwald⁷⁴ now denies that it occurs in muscle. Even when mercuric acetate is employed as precipitant in the presence of sodium carbonate, creatine is oxidised to α -methylguanidinoglyoxylic acid,⁷⁵



and this substance, on evaporation with hydrochloric acid, yields methylguanidine.

Even if methylguanidine is absent from normal muscle and urine, this enhances rather than diminishes the importance to be attached to its undoubted excretion after parathyroidectomy, which was dealt with in last year's Report.⁷⁶ For a further discussion of methylguanidine, as well as its relationship to creatine and arginine, the Presidential Address to the Physiological Section of the British Association, 1919, by D. N. Paton, should be consulted.

I have here only space to direct attention to interesting indirect support of the view⁷⁷ that arginine and histidine are largely capable of replacing one another in metabolism. This support has unexpectedly come from the purely chemical side, for R. G. Fargher

⁷⁰ "Lecithin and Allied Substances," 1918, p. 52 (Longmans).

⁷¹ P. A. Levene and C. J. West, *J. Biol. Chem.*, 1918, **33**, 111; **34**, 175; **35**, 285; *A.*, i, 98, 288, 421.

⁷² *Biochem. Zeitsch.*, 1910, **24**, 268; *A.*, 1910, i, 295.

⁷³ *Biochem. J.*, 1916, **10**, 103; *A.*, 1916, i, 528.

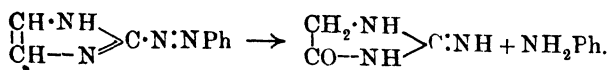
⁷⁴ *J. Amer. Chem. Soc.*, 1919, **41**, 1109; *A.*, i, 562.

⁷⁵ L. Baumann and T. Ingvaldsen, *J. Biol. Chem.*, 1918, **35**, 277; *A.*, 1918, i, 423.

⁷⁶ *Ann. Report*, 1918, 152.

⁷⁷ H. Ackroyd and F. G. Hopkins, *Biochem. J.*, 1916, **10**, 551; *A.*, 1917, i, 237. Compare also *Ann. Report*, 1918, 155.

and F. L. Pyman⁷⁸ have shown that 2-benzeneazoglyoxaline yields on reduction aniline and glycocyamidine.



It should also be remembered in this connexion that creatinine is *N*-methylglycocyamidine.

On the other hand, H. B. Lewis and E. A. Doisy⁷⁹ have assailed Ackroyd and Hopkins's conclusion that arginine and histidine are pre-eminently the raw material for the synthesis of purines. They found no difference in the uric acid output of two men maintained for successive periods on purine-free high protein diets containing (a) much arginine and histidine, (b) little of these amino-acids.

Accessory Food Substances.

The present state of our knowledge on these substances (mis-named "vitamines") has been admirably summarised by a committee consisting of F. G. Hopkins (chairman), H. Chick, J. C. Drummond, A. Harden, and E. Mellanby,⁸⁰ appointed jointly by the Lister Institute and Medical Research Committee. This report constitutes a veritable monograph of 107 pages with 18 illustrations and more than 200 references to the literature, extending to the first few months of the current year. It deals with accessory factors and growth, beri-beri, scurvy, rickets, pellagra, and practical problems relating to the diets of adults and infants. On account of the appearance of this compilation and the fact that the interest in accessory food substances is still almost entirely physiological, I propose to limit myself here to very few references. E. M. Delf⁸¹ compared, necessarily in a very crude manner, the rate of destruction of the antiscorbutic substance in cabbage on heating to 60° and to 90—100°. From the relatively low temperature-coefficient of this reaction (1.3 for 10° rise of temperature), she concludes that the destruction does not consist in the heat denaturation of a protein or enzyme. T. B. Osborne and L. B. Mendel⁸² find that certain green vegetables, for example, spinach, are rich in fat-soluble *A* even after drying at 60°, and they have succeeded in extracting the substance from dried leaves by means of ether.⁸³ The green extract was evaporated on starch, and gave a very potent

⁷⁸ *T.*, 1919, 115, 221.

⁷⁹ *J. Biol. Chem.*, 1918, 36, 1; *A.*, 1918, i, 559.

⁸⁰ "Special Report Series of the Medical Research Committee," No. 38; H.M. Stationery Office, 1919.

⁸¹ *Biochem. J.*, 1918, 12, 416.

⁸² *J. Biol. Chem.*, 1919, 37, 187.

⁸³ *Proc. Soc. Exp. Biol. Med.*, 1919, 16, 98.

preparation. The fact that this may be described as a 'distinct, advance will illustrate the very rudimentary nature of our knowledge concerning this substance. Water-soluble *B* is much more stable, and is not destroyed completely at 120° in three hours unless alkali has been added.⁸⁴ The antiscorbutic substance is readily destroyed by heat, but nevertheless cow's milk, rapidly dried at a high temperature, retains some of its antiscorbutic properties. On this important practical question a recent, careful paper by R. E. Barnes and E. M. Hume⁸⁵ should be consulted.

Enzymes and Fermentation.

The importance of adsorption as a preliminary to enzyme action may provide the excuse for a brief reference to papers by I. Langmuir,⁸⁶ who, for example, suggests that the spreading of oil on water is due to the residual valencies in the carboxyl group being held by the residual valencies of the water, so that the oil molecules lie in a single layer with their hydrocarbon chains vertically upwards. The layer is also one molecule thick in the adsorption of gases by plane surfaces of platinum, mica, and glass. Langmuir objects that in the porous substance usually worked with the surface is not known. A. M. Williams⁸⁷ has deduced a theory of gaseous adsorption which, over a long range, agrees very closely with experimental observations; it also enables one to calculate the surface of the adsorbent, and it supports the views of Langmuir and others as to the smallness of the range of molecular attraction.

Because specificity in enzyme action is closely related to the asymmetric structure of the substrate and adsorption is a necessary preliminary, C. W. Porter and C. T. Hirst⁸⁸ have prepared (racemic) dyes with an asymmetric carbon atom; these dyes are partly resolved when wool is dyed with them. The result is specially significant if we consider the dyeing process to be one of adsorption rather than of chemical action.

The action of invertase has been simulated in two ways. Sucrose is hydrolysed by dialysed colloidal silicic acid;⁸⁹ concentrated solutions of the acid soon change their degree of dispersion, become less active, and finally coagulate. Sucrose is also hydrolysed to a

⁸⁴ Compare C. Voegtlin and G. C. Lake, *Amer. J. Physiol.*, 1919, **47**, 558.

⁸⁵ *Biochem. J.*, 1919, **13**, 306.

⁸⁶ *J. Amer. Chem. Soc.*, 1916, **38**, 2221; 1917, **39**, 1848; 1918, **40**, 1361; *A.*, 1917, ii, 19, 525; 1918, ii, 430.

⁸⁷ *Proc. Roy. Soc.*, 1919, **96**, [A], 287, 298; *A.*, ii, 496.

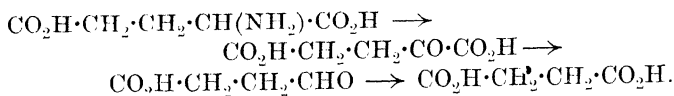
⁸⁸ *J. Amer. Chem. Soc.*, 1919, **41**, 1264; *A.*, i, 558.

⁸⁹ Albert Mary and Alexandre Mary, *Compt. rend.*, 1918, **167**, 644; *A.*, ii, 14.

slight extent (about 1 per cent.) when a solution is passed five times through a Richardson pulveriser,⁹⁰ which ionises the water mechanically; the biological interest lies in the fact that the inversion is increased in Ringer's solution, and particularly by traces of zinc or manganese, but is prevented by enzyme "poisons," such as potassium cyanide. The favourable effect of some inorganic salts and the inhibitory effect of antiseptics on the growth of *Aspergillus*, first studied by Raulin, runs also parallel to the effects of these salts and antiseptics on the inversion of sucrose, as studied by Abelous and Aloy.

Pepsin has lately been purified by L. Davis and H. M. Merker,⁹¹ who consider that the pure enzyme might be a gluco-protein. At all stages of purification, the rennetic activity corresponded closely with the proteolytic. A simple method of purifying trypsin and other enzymes has been indicated by J. T. Wood,⁹² who allows a concentrated solution to soak into filter paper, which is then rapidly dried at a low temperature. On extracting with water, the enzyme dissolves more rapidly than some impurities, and an active solution containing very little protein can be obtained.

The numerous fermentative changes which can be brought about by fungi and by yeast continue to be studied intensively. *Aspergillus niger* is found⁹³ to ferment large quantities of sucrose, with the production of 60—70 per cent. of acids, mostly fumaric with a little citric; the solution becomes acid to Congo-red. It had already been observed that *Rhizopus nigricans* (*Mucor stolonifer*) will do the same.⁹⁴ The various stages involved in the production of succinic acid from glutamic acid by yeast are, according to C. Neuberg and M. Ringer,⁹⁵ the following:



The last reaction, conversion of aldehydopropionic into succinic acid, may be brought about by maceration juice in the absence of air, and all the stages have now been shown to be purely enzymatic except the first, which is only known to occur in the living cell. The discovery of a ferment which can convert an amino-acid into the corresponding keto-acid would indeed be interesting.

Succinic acid is but one of the by-products of alcoholic ferment-

⁹⁰ J. E. Abelous and J. Aloy, *Compt. rend.*, 1919, **168**, 1125; *A.*, i, 310.

⁹¹ *J. Amer. Chem. Soc.*, 1919, **41**, 222; *A.*, i, 180.

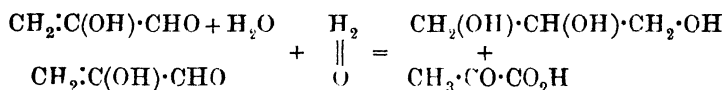
⁹² *J. Soc. Chem. Ind.*, 1918, **37**, 313T; *A.*, i, 102.

⁹³ C. Wehmer, *Ber.*, 1918, **51**, 1663; *A.*, i, 58.

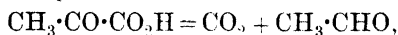
⁹⁴ F. Ehrlich, *ibid.*, 1911, **44**, 3737; *id.*, 1912, ii, 192.

⁹⁵ *Biochem. Zeitsch.*, 1918, **91**, 131; *A.*, i, 56.

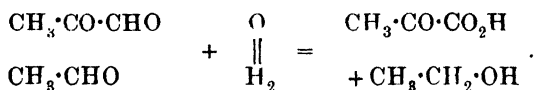
ation; glycerol is another, and a more important one, 'for it is formed from the sugar itself. During the war, this circumstance has assumed enormous importance in Germany, for it made possible the production of glycerol from sugar on an industrial scale; it was discovered that, under special conditions, the ordinary yield of glycerol of about 3 per cent. can be increased at least tenfold. Although it was known that Germany possessed a new biochemical source of glycerol, the process was kept a close secret until its publication by K. Schweizer⁹⁶ and by W. Connstein and K. Lüdecke.⁹⁷ The latter were the real authors of the industrial process,⁹⁸ the essential feature of which is the employment of concentrated sugar solutions containing a large quantity of sodium sulphite. Crude sugar, or even molasses, may be used, and neither the race of yeast nor the temperature are of much influence on the yield of glycerol. The monthly output in Germany finally amounted to 1000 tons, 100 parts of sugar yielding 20 parts of purified glycerol, 27 of alcohol, and 3 of aldehyde. The process is based on the work of Neuberg and his pupils, and he has also lately furnished a theoretical explanation in a paper,⁹⁹ which should be consulted by all interested in the theory of alcoholic fermentation. In 1913 C. Neuberg and J. Kerb¹ put forward the hypothesis that dextrose, by loss of two molecules of water, furnishes the aldol of methylglyoxal, $C_6H_8O_4$, which breaks down to two molecules of this keto-aldehyde, $C_3H_4O_2$, one of which is reduced to glycerol, whilst the other is oxidised to pyruvic acid:



The pyruvic acid is decarboxylated by carboxylase to acetaldehyde,



and the latter is reduced to alcohol, whilst from a further molecule of methylglyoxal pyruvic acid is regenerated.



⁹⁶ *Helv. chim. Acta*, 1919, 2, 167; *A.*, i, 239.

⁹⁷ *Ber.*, 1919, 52, [B], 1385; *A.*, i, 463.

⁹⁸ Compare also *J. Soc. Chem. Ind.*, 1919, 38, 287R.

⁹⁹ C. Neuberg and E. Reinfurth, *Ber.*, 1919, 52, [B], 1677; *A.*, 1920, i, 124.

¹ *Biochem. Zeitsch.*, 1913, 58, 158; *A.*, 1914, i, 118.

Hence methylglyoxal and pyruvic acid would be intermediate stages, glycerol and acetaldehyde necessarily by-products; as a matter of fact, the latter are always both present in alcoholic fermentation; the circumstance that the only known form of methylglyoxal does not ferment is no fatal objection, since it is probably the most stable of the many possible forms. (At least twenty-two are conceivable.)

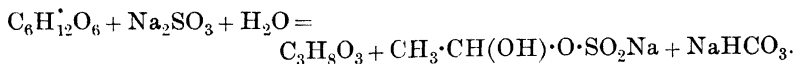
Next it was found² that slightly alkaline salts do not suppress the fermentation, but increase the yield of the by-products at the expense of the main products, and then it was shown³ that by the use of sodium sulphite the acetaldehyde may be fixed in a yield of 70 per cent. of the theoretical as the additive compound



The similar additive product of pyruvic acid undergoes decarboxylation. As the acetaldehyde is now no longer reduced, the "hydrogen of fermentation" is used up in forming more glycerol. Since the aldehyde-sulphite compound dissociates, its yield, and that of the glycerol, should depend on the concentration of the sodium sulphite employed, but not be proportional to it (mass action). The theory further demands that glycerol and acetaldehyde should be formed in molecular proportions. Both these postulates are fulfilled; thus, for 100 grams of dextrose and varying amounts of sulphite, the following yields were obtained:

Na ₂ SO ₃ used. Grams.	Yield of acetaldehyde. Grams.	Yield of glycerol. Grams.
33	11.90	23.37
50	12.52	24.86
75	13.89	27.61
150	18.65	36.90

The molecular ratio acetaldehyde:glycerol is therefore 0.94—0.95 instead of 1. The highest yield of glycerol corresponds with 35.06 per cent. of hexose, or 70 per cent. of the moiety which could furnish glycerol. For a 100 per cent. conversion, the fermentation would have to proceed completely according to the equation



The shortage of 30 per cent. is due to unsuppressed dissociation of aldehyde-sulphite. With the same relative quantities of sugar

² C. Neuberg and E. Färber, *Biochem. Zeitsch.*, 1916, **78**, 238; *A.*, 1917, i, 502.

³ C. Neuberg and E. Reinfurth, *ibid.*, 1918, **89**, 365; *A.*, 1918, i, 517; *Ann. Report*, 1918, 166.

and sulphite in dilute solution, the dissociation is much greater and the yield of glycerol falls off considerably. In their most recent paper, Neuberg and Reinfurth state that insoluble calcium sulphite suspended in the fermenting solution has advantages over the sodium salt. As calcium sulphite has a neutral reaction, it seems that alkalinity is not an essential condition for an increased production of glycerol.

GEORGE BARGER.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

ALTHOUGH 1919 will scarcely rank among the years of great achievements in agricultural chemistry, it has been notable for some highly promising developments. Chief among these, as far as this country is concerned, is the intention of the Board of Agriculture, as announced in the Press, to set aside the sum of £2,000,000 for agricultural education and research during the next five years, of which £250,000 will be available for research. Although this sum divided among ten or twelve institutions and spread over five years does not at the present value of money represent affluence, it is, nevertheless, a highly important advance on anything previously attempted in this country.

Another significant event is the establishment by an important agricultural company—the Olympia Co., under the chairmanship of Mr. Joseph Watson—of a research laboratory under the able guidance of Professor C. Crowther, late of the Leeds University. He has already secured the services of two of the best of the younger men, Mr. C. T. Gimingham of the University of Bristol Agricultural Research Station, and Mr. H. Hunter of the Irish Department of Agriculture. Apart from investigations incidental to its advisory work for the Company, the department will be specially equipped for work on animal nutrition, plant breeding, and problems of soil and plant nutrition.

Soil Investigations.

The investigations on soil in recent years have fallen in the main into three great groups, dealing respectively with (1) the solution with which the soil is moistened, (2) the population of micro-organisms living on the plant residues which form an important part of the soil, and (3) the biochemical conditions in the soil. Hitherto these investigations have been on widely different lines, but there seems now the possibility of a closer approximation.

The importance of the soil solution in the nutrition of crops was

first adequately recognised by Whitney and Cameron, working in the United States at Washington. The more recent work has been done at the California Experiment Station. The general outlines of the earlier work were given in last year's Report, and two further papers have been published this year. A careful study has been made of the relation of the concentration and reaction of the nutrient medium to the growth of the plant.¹ The rate of growth of barley in water cultures was found to increase with increasing concentration up to a certain point, beyond which there was no further growth. The amount of substance absorbed, however, increased with the concentration to a greater extent and over a longer range than did the growth. Contrary to some of the previous work, no sufficient evidence was found that plants require any very definite ratios of elements or ions; indeed, considerable limits of variation seemed permissible so long as the total supply and concentration of the elements were adequate. Working on rather different lines, and in soil instead of water cultures, J. S. Burd² finds that the absorption of various nutrients by barley growing in soil increases rapidly up to the ninth week, and then a reversal takes place, there being a loss of material from the aerial parts of the plant to the root, or even to the soil, although no actual transfer to the soil can be definitely established. After the eleventh or twelfth week, however, there is a further absorption which continues to the end of the growing period, when a further loss appears to set in.

The solution moistening the soil particles has been extracted by various methods, and it has also been studied in the soil by the freezing-point method, more particularly by Bouyoucos and his colleagues.³ Perhaps the most interesting paper on the subject during the year has been a discussion⁴ of the numerous data already accumulated. Previous investigators have shown that the soil solution in quartz sand and in very light sandy soils obeys approximately the same law as dilute solutions, the freezing-point depression varying as the concentration. In the case of ordinary soils, however, this rule does not hold, the freezing-point depression increasing more rapidly than the moisture content falls off. Bouyoucos explained the discrepancy by supposing that some of the soil moisture plays no part in the phenomena of the depression of the freezing point, and he deducts from the total moisture

¹ D. R. Hoagland, *J. Agric. Res.*, 1919, 18, 73.

² *Ibid.*, 1919, 18, 51.

³ G. J. Bouyoucos and M. M. McCool, *Michigan Agric. Coll. Expt. Station Tech. Bulls.* 24, 31, 36, 37 and 42¹; also *J. Agric. Res.*, 1918, 15, 331; *A.*, i, 115.

⁴ B. A. Keen, *J. Agric. Sci.*, 1919, 9, 400.

a sufficient amount, which he calls the "unfree water," to leave a balance of "free water" that will conform to the freezing-point law. Assuming the distinction to be valid, Keen shows that a mathematical relationship exists between the "free," the "unfree," and the total water; one equation defines the relationship over the whole range. Exactly the same thing happened in regard to the rate of evaporation of water from soils; one equation there also covered the whole range, and the various constants and critical points announced by other workers were found to be equilibrium points only, and not breaks in the physical state of the water in the soil.⁵

The physical properties of the soil are determined by its peculiar structure: a mass of small, hard, mineral particles of varying dimensions intimately associated with a sufficient quantity of colloidal matter to impress colloidal properties on the whole. The relationships of adsorption to coagulation have been discussed by some of the Italian workers.⁶ Setting out from the obvious proposition that mutual attraction occurs where particles and ions with opposite charges come into contact, resulting in the neutralisation of the charges and formation of absorption compounds, the authors attempt to show that the consequent decrease in concentration, both in colloidal and ionic-molecular solution, is favourable to productivity. The phenomena in regard to protein have been discussed by the Wilsons,⁷ but they are not necessarily related to the soil phenomena. The problem has been attacked in another way in Germany.⁸ A salt is allowed to act on a soil, and is then extracted with water and the effect on the physical properties studied. Salts of univalent metals, particularly sodium salts, damage the texture of the soil; those of bivalent metals do not. In this case, however, the effects are not so much those of the actual salt as those produced by the subsequent hydrolysis after the salt is washed away.

An attempt has been made⁹ to ascertain the effect of certain colloidal substances on the growth of wheat seedlings in culture solution. They acted adversely, reducing the concentration by adsorption. Colloidal silica, however, proved to be an exception, and caused an increase not only in growth but also in the amount of silica in the plant.

⁵ *J. Agric. Sci.*, 1914, **6**, 456.

⁶ A. de Dominicis and P. Chiarieri, *Staz. sper. agr. ital.*, 1917, **50**, 451; *A.*, i, 142.

⁷ J. A. Wilson and W. H. Wilson, *J. Amer. Chem. Soc.*, 1918, **40**, 886; *A.*, 1918, ii, 260.

⁸ G. Hager, *J. Landw.*, 1918, **66**, 241.

⁹ D. S. Jennings, *Soil Sci.*, 1919, **7**, 201.

*The Biochemical Changes in the Soil.*⁶

The soil organisms draw their supplies of food material and of energy from the stores of plant residues contained in the soil. The two most important constituents of the plant residues are the cellulose and the proteins; the former give rise to the so-called humus which has important physical effects in the soil; the latter yield ammonia, which becomes subsequently oxidised to form the nitrates essential to the nutrition of the crop.

The organism concerned in the decomposition of cellulose has been studied¹⁰ in the Rothamsted laboratories. It decomposes cellulose under aerobic conditions with comparative ease. It more closely resembles the spirochaëts than the bacteria, and is therefore named *Spirochaeta cytophaga*. Its vegetative growth takes the form of a sinuous filamentous cell, which is very flexible, but only feebly motile; apparently it does not possess flagella. This filamentous form can pass through a number of phases, yielding finally spherical bodies somewhat resembling spores, but differing in several important respects, so that they are called by a different name, sporoids. The organism requires combined nitrogen, which it prefers in the form of nitrates, ammonium salts, amides, or amino-acids. Peptone serves in dilute solutions, but a toxic limit is soon reached, whilst the conventional nutrient gelatin and nutrient agar are both unsuitable.

The carbon requirements of the organisms can be met only by cellulose so far as is known. None of the sugars, alcohols, or salts of organic acids has proved effective, and some were definitely toxic.

Given a suitable simple nitrogen compound and its other requirements, the organism is able energetically to decompose cellulose, producing, among other things, a pigment somewhat like carotin, a mucilage which does not yield optically active compounds on hydrolysis, and small quantities of volatile acids. It was shown that the products are suitable for the needs of *Azotobacter* and allow of the assimilation of gaseous nitrogen.

The decomposition of the proteins is brought about by bacteria and apparently also by fungi, although on the latter point evidence is still scanty. Fungi have been isolated in considerable numbers from soils, and their behaviour towards culture media has been studied. Thus it has been shown¹¹ that they decompose carbohydrates, absorbing ammonia and producing protein, although in absence of carbohydrates they decompose protein, forming ammonia. It is argued that moulds are likely to be unfavourable to soil

¹⁰ H. B. Hutchinson and J. Clayton, *J. Agric. Sci.*, 1919, 9, 143.

¹¹ S. A. Waksman, *Soil Sci.*, 1918, 6, 137; *A.*, i, 116.

fertility, except perhaps in so far as the formation of enzymes in the soil is concerned. The difficulty is that the fungi are a plastic group which may behave in one way under one set of conditions, but quite differently, under other conditions. Evidence, however, has been adduced that fungi may be positively harmful.¹²

Pending further investigations into the part played by the fungi, it is usual to confine attention to bacteria. In recent years bacteriologists have been content to study "ammonification" as a whole without much reference to the individual species of organisms concerned. A few attempts, however, have been made at studying the individual species. In the United States H. J. Conn¹³ finds that non-spore formers predominate in the soil, thus confirming the observations of Russell and Hutchinson at Rothamsted; he considers that spore-formers are scarcely active in the soil under normal conditions, and that ammonia formation is mainly brought about by non-spore formers (*Tech.*, 51). In this he runs counter to the accepted tradition, which is that the spore formers include some of the most active forms. Marchal had concluded that *B. mycoides* was one of the most common ammonia producers in the soil. Conn controverts this statement, and maintains that of the eight important ammonifiers studied by Marchal only one, namely, *B. fluorescens liq.* (a non-spore former), is a typical soil organism.

Of the true soil organisms two are described¹⁴ which, whilst not very numerous in unmanured soil, multiply vigorously on addition of farmyard manure and produce ammonia: *Ps. fluorescens* and *Ps. caudatus*. These organisms are described in sufficient detail to allow of identification by other workers.

It is further shown¹⁵ that the *Actinomycetes* form a considerable proportion of the soil organisms—no less than 17 per cent. in a medium soil, and a higher proportion in heavy soils or those rich in organic matter.

An interesting study has been made¹⁶ of the rate at which nitrates accumulate in Egyptian soils under natural conditions. Normally, the process yields more nitrate than the crop requires, which may account for the usual ineffectiveness of nitrogenous manures on the cotton crop in Egypt. The rate of nitrification, however, was much affected by the moisture content of the soil—more, indeed, than by any other single factor—and the whole process apparently came to

¹² E. B. Fred, *Soil Sci.*, 1918, 6, 333.

¹³ N. Y. Cornell, *Agric. Expt. Sta. Bull.*, 338, 1913; *Tech. Bull.* 51, 1916; *Tech. Bulls.* 57–60, 1917, and 64, 1918; *J. Agric. Res.*, 1919, 16, 313.

¹⁴ H. J. Conn and J. W. Bright, *J. Agric. Res.*, 1919, 16, 313.

¹⁵ S. A. Waksman and R. E. Curtis, *Soil Sci.*, 1918, 6, 309.

¹⁶ J. A. Prescott, *J. Agric. Sci.*, 1919, 9, 216.

a standstill during the summer fallow, a time of low moisture content and high temperature. In pot experiments there was more nitrate produced under fallow conditions than in the presence of a growing crop, as has already been observed both in England and America.

It has always been supposed that the nitrogen cycle was comparatively simple, the soil nitrogen compounds being changed to nitrates, which, unless washed out of the soil, are then absorbed by plants and built up into fresh protein compounds. The results of a long-continued soil experiment at Rothamsted are now summarised, and show¹⁷ that this simple view is scarcely sufficient; the nitrate formation in a poor, unmanured soil, so far as can be measured by the quantity washed out in drainage water, proceeds at a very slowly diminishing rate for an almost indefinite period—certainly for more than fifty years—and during this time it appears almost uniform over a period of, say, from ten to fifteen years. The simplest explanation of the phenomena is that the nitrates formed in any one year are not wholly available for the plant or for loss in the drainage water; a part may be supposed to be taken up at once by other organisms and converted into protein, which subsequently again nitrifies. Thus the whole of the nitrate can never be exhausted; the process is expressible by an asymptotic curve. This idea of an immobiliser will probably be found helpful in dealing with the soil phenomena.

There is, however, a further complication in natural conditions. For convenience of investigation the decomposition of cellulose and of protein are studied separately, but in point of fact the two reactions proceed simultaneously in the soil and profoundly influence each other. It has already been shown that the organisms decomposing cellulose require a supply of nitrate or other soluble nitrogenous compound. In like manner organisms decomposing sugar apparently require nitrates, and there is, in addition, the possibility that they actually decompose nitrates with evolution of gaseous nitrogen or nitrogen compounds.

Both these actions tend to loss of nitrogen. There is a third type of action that tends to a gain of nitrogen. In the presence of easily oxidisable carbohydrates certain organisms can fix gaseous nitrogen, converting it into protein, which subsequently decomposes and gives rise to ammonia, and then to nitrates.

Thus the addition of sugar or straw to the soil has a drastic effect on the nitrogen cycle, the possibilities being a loss of nitrate in two ways and a gain of protein in two ways—an absolute gain from free nitrogen and a relative gain from nitrate or ammonia. Whether

¹⁷ E. J. Russell and E. H. Richards, *J. Agric. Sci.*, 1919, 10, 14.

the net change will be a gain or less of nitrogen depends on circumstances. Thus in recent experiments the addition of 2 per cent. of sugar to soil was found¹⁸ to diminish the first crop, but slightly to increase the subsequent ones. Straw diminishes the crop for the first two years, but gave a small increase in the third year; over the whole period, however, the effect was negative.

These various actions make it impossible to foretell the fate of a green crop ploughed into the soil—a practice known as green manuring, common in this country, in India and elsewhere. In a recent Indian investigation,¹⁹ the stems and roots of leguminous plants were found to yield scarcely any nitrate, presumably because of the action of their non-nitrogenous constituents. Further, there were marked differences in the rates of nitrification of some of the oil cakes.²⁰

The importance of the changes effected by micro-organisms is so great that numerous attempts have been made to correlate soil fertility with bacterial activity, as indicated by rates of ammonification, nitrification, etc. Obviously correlation can be expected only when the nitrogen supply is a limiting factor in crop production, and even then regard must be had to the supplies in the soil of protein compounds on which the organisms can act. With these limitations, however, some relationship between bacterial activity and soil fertility is generally found. In a detailed examination of Hawaiian soils,²¹ the rate of ammonification afforded no sharp indication of fertility, as the differences between the good and the poor soils, although in the right direction, were not sufficiently marked. On the other hand, the rate of nitrification was a much safer index, and was, indeed, the most trustworthy of all the methods tested; this experience has been obtained elsewhere.²² This does not imply that the process of nitrification is responsible for the yield; it may be that both the plant and the nitrifying organisms are limited by the same set of factors.

Effect of Salts.—The effect of inorganic salts on bacterial activity has been investigated by Greaves and his colleagues at the Utah Expt. Station,²³ where alkali soils present troublesome problems.

¹⁸ O. Lemmermann and A. Einecke, *Landw. Versuchs-Stat.*, 1919, **93**, 209.

¹⁹ N. U. Joshy, *Agric. J. India*, 1919, **14**, 395.

²⁰ F. J. Plymen and D. V. Bal, *ibid.*, 414.

²¹ P. S. Burgess, *Soil Sci.*, 1918, **6**, 449.

²² For example, in Kansas by P. L. Gainey, *ibid.*, 1917, **3**, 399; A., 1917, **i**, 529; in Pennsylvania by G. P. Given, *Penn. Rept.*, 1912-13, 204; in California by C. B. Lipman and Burgess, *Cal. Bull.* 260, 107; in Iowa by P. E. Brown, *J. Agric. Res.*, 1916, **5**, 855.

²³ J. E. Greaves, E. G. Carter, and H. C. Goldthorpe, *J. Agric. Res.*, 1919, **16**, 107; A., **i**, 238.

The method consists in adding 2 per cent. of blood meal to the soil, then bringing up the moisture to 20 per cent., and finally incubating at 28—30° for twenty-one days. The conditions obviously are unnatural, and it would have been interesting to have made the comparison also under normal conditions. Nevertheless, the results are distinctly interesting. The effects of the various salts in depressing the activity of the ammonifying organisms are in the main similar to their action in depressing the growth of wheat seedlings. The effect on nitrifying organisms, however, is more pronounced. The salts commonly occurring in alkali soils, sodium sulphate, sodium carbonate, and calcium chloride, are very toxic to bacterial activity, and hence the possibility that part of the unsuitableness of an alkali soil for plant growth may lie in the depression of the essential nitrate production process.

Nitrogen fixation is also affected considerably by the presence of dissolved salts.²⁴ Sodium chloride in small quantities acted as a stimulant, but at and above a concentration of 0.01 per cent. a falling off in activity occurred. Sodium nitrate, on the other hand, caused distinct increase in the amount of fixation.

The effect of salts appears to be specific, and not osmotic. Calcium sulphate markedly stimulates nitrification, as has been observed before under other conditions; so also did sodium chloride, magnesium carbonate, and sodium carbonate²⁵ in appropriate concentrations, although beyond the proper limits harmful effects have been produced. On the other hand, calcium carbonate was found to be toxic, an observation that deserves to be followed up in view of the known beneficial effect of this substance on fertility.

The effect of nitrates on soil organisms is of special importance, because of the possibility that they may serve as nutrients. The nitrates of sodium, magnesium, manganese, calcium, and iron actively stimulate nitrogen-fixing organisms. They also stimulate certain organisms which assimilate nitrates, transforming the nitrogen into protein; thus, in the conditions of these experiments, they actually led to a decrease of nitric nitrogen in the soil. Further, Hutchinson and Clayton have found that they increase very considerably the growth of the spirochaets which decompose cellulose. On the other hand, sodium nitrate appears to depress nitrification,²⁶ but as it caused a loss of nitrate from the medium,

²⁴ T. M. Singh, *Soil Sci.*, 1918, 6, 463; A., i, 374.

²⁵ T. M. Singh, *loc. cit.*, but Greaves obtained no stimulating action with sodium carbonate.

²⁶ T. M. Singh, *Soil Sci.*, 1918, 6, 463; A., ii, 374.

the effect may have been simply the stimulation of nitrate-assimilating organisms already referred to.

Numerous investigations have been made in the United States into the effect of the chains of bacterial processes on the mineral constituents of the soil. The nitrification of dried blood and the bacterial oxidation of sulphur in mixtures of sand and felspar are accompanied by an increase in the amount of water-soluble potash;²⁷ the increase, however, is considered to be brought about by the salts formed, especially by ammonium sulphate, rather than by direct action of acid on the insoluble potassium compounds. Previous investigation has shown that both these changes, when carried out in culture solution,²⁸ increase the solubility of rock phosphate. It is now shown²⁹ that no solvent action on phosphate accompanies nitrification in the soil, nor did any accompany bacterial oxidation of sulphur, excepting in the case of acid soils. Ammonium sulphate, however, has little or no solvent action on rock phosphate, so that on the author's hypothesis the facts are explicable.

These secondary actions of substances on soil constituents have been invoked to explain some of the curious effects produced when mixtures of fertilising constituents are used.³⁰ Instances are quoted where an insoluble phosphate by itself was less effective as a fertiliser than a soluble phosphate, although on the addition of sulphate of ammonia it became equally effective. There is some disagreement as to the precise facts, but the possibility of these secondary actions seems worth exploring.

An interesting suggestion has been made³¹ for the practical utilisation of the bacterial oxidation of sulphur in soils. Potato growers prefer an acid soil, because acidity, whilst not unfavourable to the potato crop, is entirely unsuited to the scab organism,³² one of its worst pests. Other crops of the rotation, however, especially clover, are injured by the acidity. It is proposed, therefore, that a dressing of 300 to 1000 lb. per acre of sulphur should be made before planting the potatoes, to ensure the requisite degree of acidity, and, after the crop is removed, sufficient lime can be added to ensure neutrality.

An important addition to our knowledge of the soil protozoa has

²⁷ J. W. Ames and G. E. Boltz, *Soil Sci.*, 1919, 7, 183.

²⁸ Hopkins and Whiting (*Illinois Bull.*, 1916, No. 190, 395) state that 115 parts of phosphorus become soluble in water for each 56 parts of nitrogen oxidised. These experiments were done in culture solution.

²⁹ J. W. Ames and T. E. Richmond, *Soil Sci.*, 1918, 6, 351.

³⁰ J. E. Greaves and E. G. Carter, *ibid.*, 1919, 7, 121; *A.*, i, 564.

³¹ J. G. Lipman, *ibid.*, 181.

³² L. J. Gillespie and L. A. Hurst, *ibid.*, 1918, 6, 219; *A.*, i, 115.

been made by D. W. Cutler,³³ who has shown that these organisms adhere firmly to the soil particles up to a certain number per gram of soil, beyond which they no longer adhere, but can float away. Each of the soils examined had a definite saturation point. If a soil is shaken with suspensions of protozoa of varying concentrations, the absorption is complete in all cases where the numbers are below the saturation capacity, but it is not extended when the numbers rise beyond. Thus the phenomenon exactly resembles in its sharpness the neutralisation of an acid with a base, and differs entirely from adsorption, which is not, in general, complete, but depends on the relative masses of the absorbed and absorbing substances.

The general biochemical conditions in the soil are frequently under investigation as being equally important to the soil organisms and to the growing crop. Among the most important is the reaction of the soil, whether acid or neutral, the acidity being measured by the hydrogen-ion concentration and by some titration method. A large number of titration methods have been devised and tested, and new series of tests and new modifications have recently been proposed.³⁴ Criticisms of the sugar method described in last year's Report have also been made.³⁵ The soil acidity is found to vary with the moisture conditions of the soil, but the variation is attributed to chemical rather than physical changes.³⁶

The supply of organic matter is of considerable importance. A remarkable effect of farmyard manure on the clover crop will be mentioned later. Another and wholly different effect is to reduce the harmful action of salts in alkali soils;³⁷ this is attributed to adsorption of the salts by the colloidal substances of the farmyard manure.

A further important effect, no doubt colloidal also, of organic matter is to increase the water-holding capacity of the soil. This is clearly marked at Rothamsted, where 15 tons of farmyard manure are added annually to certain plots; it does not show, however, in the Minnesota investigations, where only 5 tons of manure had been added each four years.³⁸

In view of these and other important properties, various means of estimating the so-called humus in soil have been suggested from

³³ *J. Agric. Sci.*, 1919, 9, 430.

³⁴ C. J. Lynde, *Trans. Roy. Soc. Canada*, 1918-9, [iii], 12, III, 21; *A.*, ii, 376; L. P. Howard, *Soil Sci.*, 1918, 6, 405; R. E. Stephenson, *Soil Sci.*, 1918, 6, 37; E. T. Wherry, *J. Washington Acad. Sci.*, 1919, 9, 305; *A.*, i, 428.

³⁵ L. T. Sharp and D. R. Hoagland, *Soil Sci.*, 1919, 7, 196.

³⁶ S. D. Conner, *J. Agric. Res.*, 1918, 15, 321; *A.*, i, 115.

³⁷ C. B. Lipman and W. F. Gericke, *Soil Sci.*, 1919, 7, 105.

³⁸ F. J. Alway and J. R. Neller, *J. Agric. Res.*, 1919, 16, 263.

time to time, a rapid test being the amount of chlorine liberated from a solution of sodium hypochlorite.³⁹

The supply of mineral matter is of recognised importance, but less work than usual has been done in recent years. The method of using weak acids for analytical purposes, general in this country, has been found satisfactory⁴⁰ in Germany also. It has been shown that the unsuitability of certain Minnesota prairie soils to leguminous crops, vaguely attributed to "rawness," is simply due to lack of mineral nutrients.⁴¹

A study has been made of the marked changes produced by heating the soil on its properties as a medium for the growth of plants and organisms.⁴²

Soil Constituents and Soil Surveys.

The soils of North Wales have been studied in detail during the past few years.⁴³ The sedentary soils of the carboniferous and millstone grit formations, which occur in the drier parts of the region, resemble those found elsewhere in that the coarsest fractions are the richest in silica; they are, however, quite unlike the sedentary soils of the palæozoic series in the wetter districts where this rule does not hold.

The organic phosphorus compounds⁴⁴ of soil and the aldehydes⁴⁵ present in the soil have received some attention.

Of the inorganic constituents, the clay is distinctly unfortunate in its name, inasmuch as the same word is used in a wholly different sense by the ceramic investigators, whose work otherwise ought to be very helpful to soil investigators.⁴⁶

The chief chemical property of "clay" (using the word, not in the ceramic, but in the soil investigator's sense) is its reactivity with salts; it readily exchanges bases. The action is not yet fully

³⁹ L. Lapique and E. Barbé, *Compt. rend.*, 1919, **168**, 118; *A.*, i, 116.

⁴⁰ O. Lemmermann, A. Einecke, and L. Fresenius, *Landw. Versuchs-Stat.*, 1916, **89**, 81; *A.*, i, 616; 1 per cent. citric acid was used for estimation of the phosphate, and 10 per cent. hydrochloric acid for estimation of the potash.

⁴¹ P. R. McMiller, *Soil Sci.*, 1919, **7**, 233.

⁴² J. Johnson, *ibid.*, 1.

⁴³ G. W. Robinson and C. F. Hill, *J. Agric. Sci.*, 1919, **9**, 259.

⁴⁴ C. J. Schollenberger, *Soil Sci.*, 1918, **6**, 365; *A.*, ii, 168; R. S. Potter and R. S. Snyder, *ibid.*, 1918, **6**, 321; *A.*, i, 142.

⁴⁵ J. J. Skinner, *J. Franklin Inst.*, 1918, **186**, 165, etc.

⁴⁶ See, for example, R. E. Somers (*J. Washington Acad. Sci.*, 1919, **9**, 113), for a mineralogical examination of "clay" corresponding with "fine sand" and "silt" in soil work.

understood, and consequently soil investigators watch with interest the work done on basic exchange in zeolites, silicates, etc., to see what light, if any, is thrown on their own problems. Among such investigations may be mentioned those of Ramann,⁴⁷ who fully realises the conditions obtaining in the soil.

The various methods of soil analysis have been discussed and compared by Richter.⁴⁸

Rain.

For many years agricultural chemists were very interested in the composition of rain-water, particularly in the amount of nitrogen compounds present, these being supposed to contribute to the nutrition of the crop. It is now recognised that the quantities present are too insignificant to exert any appreciable effect, and the long-continued series of analyses at Rothamsted have been discontinued. The results have been summarised.⁴⁹ The ammoniacal nitrogen amounts on an average to 0.405 part per million, corresponding with 2.64 lb. per acre per annum; the yearly fluctuations in lbs. per acre follow the rainfall fairly closely. The nitric nitrogen (which includes nitrites) is on an average one-half of this amount, namely, 1.33 lb. per acre per annum. There is a marked difference in composition between summer and winter rainfall, suggesting that they may differ in their origin; the winter rain resembles Atlantic rain in its high chlorine and low ammonia and nitrate content; the summer rain is characterised by low chlorine but high ammonia and nitrate content, suggesting that it arises by evaporation of water from the soil and condensation at higher altitudes than in the case of winter rain. Whilst the subject has no obvious agricultural interest, there is the possibility of a useful continuation of the work in connexion with atmospheric pollution.

It is interesting to note that the quantity of ammonia and nitrate collected in the rain at Ottawa⁵⁰ is of the same order as at Rothamsted, namely, 0.46 part per million of free ammonia, 0.138 as albuminoid ammonia, and 0.277 as nitrite and nitrate, making, with the organic nitrogen, 6.58 lb. per acre of nitrogen, as against a little more than 5 at Rothamsted. Very similar results were obtained at Cornell,⁵¹ where the average free ammonia was 0.407,

⁴⁷ E. Ramann and A. Sprengel, *Zeitsch. anorg. Chem.*, 1919, **105**, 81; A., i, 615. See also G. Kornfeld, *Zeitsch. Elektrochem.*, 1917, **23**, 173; A., ii, 459; I. Zoch, *Chemie der Erde*, 1915, **1**, 55 pp.; A., ii, 470.

⁴⁸ G. Richter, *Int. Mitt. Bodenkunde*, 1916, **6**, 193, 318; A., 1918, ii, 280.

⁴⁹ E. J. Russell and E. H. Richards, *J. Agric. Sci.*, 1919, **9**, 309.

⁵⁰ F. T. Shutt and R. L. Dorrance, *Trans. Roy. Soc. Canada*, 1917-18, [iii], **11**, 63; A., i, 116.

⁵¹ J. E. Trieschmann, *Chem. News*, 1919, **119**, 49; A., i, 511.

the albuminoid ammonia 0.366, the nitrate 0.255, and the nitrite 0.018 part per million respectively.

Fertilisers and Manures.

In the main, investigations this year have been concerned with details of importance to the technical chemist and the agricultural adviser; they are dealt with in the Report to the Society of Chemical Industry, and need not, therefore, be discussed here. The organic manures have been under investigation, and one or two conclusions of general interest have emerged. Farmyard manure has been shown⁵² to exert a beneficial effect on the growth of clover, apparently greater than its composition leads one to expect; this result may be related to the life-cycle of the organism, which is now under investigation.

Other organic substances used as manure include rape cake (the residue left after the extraction of oil from rape seed); this contains a considerable proportion of plant protein, the decomposition of which in the soil gives rise to nitrates. It is often supposed that plant or animal proteins must necessarily be more useful as fertilisers than nitrates; this anticipation does not appear to be correct.⁵³

An investigation has been made into the power of calcium sulphate to "fix" part of the ammonia liable to be lost from manure heaps;⁵⁴ whilst this shows that some degree of conservation may be possible, it does not throw light on the fertilising value of the mixture of farmyard manure and calcium sulphate. In the case of liquid manure, gypsum was only partly effective.⁵⁵

Sulphates are not regarded as fertilisers in this country, although considerable quantities are, as a matter of fact, applied to crops in the form of ammonium sulphate and superphosphate. It is known, however, that sulphur is essential to crops, and an interesting case is recorded from Oregon⁵⁶ of soils responding markedly to sulphur and sulphates, larger returns having been obtained from gypsum than from lime. Both sulphur and sulphates gave increased yields of oats, rape, and red clover, and in the latter case they led to more nodule formation.

⁵² E. J. Russell, *J. Bd. Agric.*, 1919, **26**, 124.

⁵³ *Idem.*, *ibid.*, 228.

⁵⁴ F. E. Bear and A. C. Workman, *Soil Sci.*, 1919, **7**, 283; *A.*, i, 511.

⁵⁵ O. Lemmermann and H. Weissmann, *Landw. Jahrb.*, 1918, **52**, 297.

⁵⁶ H. G. Miller, *J. Agric. Res.*, 1919, **17**, 87; *A.*, i, 510.

The Absorption of Nutrients by the Plant Roots.

The nutrient materials derived from the soil are absorbed by the root, and numerous investigations have been made into the mechanism of the process. W. Stiles and F. Kidd⁵⁷ measured the changes in conductivity of the solution of a salt presented to the plant tissue; these were taken to measure the rate of absorption. Absorption at first was approximately proportional to the external concentrations; as it progresses, however, it tends towards an equilibrium expressible by the ordinary adsorption equation. Nevertheless, the authors wisely refrain from regarding the whole process as necessarily an adsorption.

A full discussion of this interesting subject lies outside the scope of the present report; it has, however, formed the subject of several other investigations.⁵⁸

Plant Nutrition.

It has always been supposed that green plants required only about a dozen elements for perfect nutrition, namely, carbon, hydrogen, oxygen, nitrogen, phosphorus, sulphur, potassium, calcium, magnesium, sodium, and iron. P. Mazé, during the past few years, has been adding to this list, and claims as a result of his recent investigations⁵⁹ that traces of the following are required in addition: boron, fluorine, iodine, chlorine, silicon, aluminium, manganese, and zinc. On the other hand, he found no necessity for organic substances, although some of them were helpful. The traces required *must* be very small, since it is a common experience at Rothamsted to obtain a copious and normal growth of barley in water cultures containing the purest obtainable salts of the conventional nutritive elements. Even if they are not essential, the elements in Mazé's list appear to be beneficial in certain circumstances, according to evidence which is steadily accumulating; during this year, for instance, investigations have been published showing the beneficial effects, under certain conditions, of compounds of fluorine,⁶⁰ silicon,⁶¹ aluminium,⁶² manganese,⁶³

⁵⁷ *Proc. Roy. Soc.*, 1919, [B], **90**, 448; *A.*, i, 240. The carrot proved very suitable for the purpose.

⁵⁸ M. Williams, *Ann. Bot.*, 1918, **32**, 591; *A.*, i, 59; W. J. V. Osterhout, *J. Biol. Chem.*, 1918, **36**, 485, 489, 557; *A.*, i, 111, 112; F. E. Lloyd, *Trans. Roy. Soc. Canada*, 1917-8, [iii], **11**, 133; *A.*, i, 111.

⁵⁹ *Ann. Inst. Pasteur*, 1919, **33**, 139; *A.*, i, 304.

⁶⁰ A. Gautier and P. Clausmann, *Compt. rend.*, 1919, **168**, 976; **169**, 115. *A.*, i, 371, 512.

⁶¹ D. S. Jennings, *Soil Sci.*, 1919, **7**, 201.

⁶² J. Stoklasa and others, *Biochem. Zeitsch.*, 1918, **91**, 137.

⁶³ *Idem.*, loc. cit.; E. P. Deatrick, *Cornell Univ. Agric. Exp. Sta. Mem.*, 1919, **19**, 371; *A.*, i, 428.

barium, and strontium.⁶⁴ In addition, traces of iodine have been found in plants growing under natural conditions.⁶⁵

Copper appears to be widely spread in the vegetable kingdom, and analyses have been made to determine how much is present in soil. About 2 to 5 milligrams per kilo. of fine earth were found in normal soils, but much higher amounts—200 or 250 milligrams per kilo.—in vineyard soils, where copper sprays are used. It is not suggested that the copper is beneficial, although small amounts probably do no harm.⁶⁶ The suggestion that selenium is a definite constituent of animals and plants, brought forward two years ago,⁶⁷ has now been called in question.⁶⁸

An important development of the scientific principles of manuring was made some time ago by E. A. Mitscherlich in the introduction of efficiency factors (*Wirkungsfactoren*) of manures. It is now shown⁶⁹ that in the case of mixtures of fertilisers, the factors remain constant so long as the constituents are without mutual action, but they vary as soon as interaction takes place. It has further been shown that, in the case of two nitrogenous manures, namely, ammonium sulphate and sodium nitrate, the ratio of the respective efficiency factors is the same whether they are calculated for corn or for straw.

Between nutritive effects and toxicity the margin seems to be narrow, and almost all of the elements essential to plant nutrition are capable of producing toxic effects under other conditions. Even so definite and essential a plant nutrient as a soluble phosphate is reported to be sometimes poisonous. Moreover, these effects have no relation to the needs of the plant; on the contrary, it has been suggested that substances of which a plant stands most in need are capable of exerting the greatest toxic effect. Thus, excess of soluble phosphate injures buckwheat, but apparently not oats; yet buckwheat is more dependent upon phosphatic manure than oats.⁷⁰ Lupins afford a similar case; they greatly need lime, and yet are easily affected adversely by it.

So ammonium sulphate, a recognised and important fertiliser, is

⁶⁴ J. S. McHague, *J. Agric. Res.*, 1919, **16**, 183; *A.*, i, 303.

⁶⁵ E. Winterstein, *Zeitsch. physiol. Chem.*, 1918, **104**, 54; *A.*, i, 190.

⁶⁶ L. Maquenne and E. Demoussy, *Compt. rend.*, 1919, **169**, 937.

⁶⁷ T. Gassmann, *Zeitsch. physiol. Chem.*, 1916, **97**, 307; 1917, **100**, 182; *A.*, 1916, i, 772; 1917, ii, 540.

⁶⁸ R. Fritsch, *ibid.*, 1918, **104**, 59; *A.*, i, 191.

⁶⁹ *Landw. Jahrb.*, 1918, **52**, 279; *A.*, i, 143. An account of these factors is given by E. J. Russell, "Soil Conditions and Plant Growth," 3rd Edition, 1917, pp. 23 *et seq.*

⁷⁰ T. Pfeiffer, W. Simmermacher, and M. Spangenberg, *Landw. Versuchs-Stat.*, 1916, **89**, 203.

capable under certain conditions of exerting toxic effects on the plant, and ammonium chloride is said to be even more toxic.⁷¹ In practice, these effects are not obtained unless the soil is acid.

It is, however, particularly characteristic of all the growth-promoting elements, other than the conventional nutritive elements, that their good effects are obtained only within very narrow limits, above which harmful effects are produced.

This narrow margin between toxicity and growth-promotion makes it very difficult to ascertain with certainty the effects of some of the constituents of the plant. It is not difficult to show in water cultures the toxicity of vegetable alkaloids and related substances to young plants.⁷² These are not, however, the conditions under which the substances act in the plant, and it is unsafe to argue that toxicity in water cultures proves toxicity in natural conditions. Some are known under other conditions to increase growth; thus, guanidine was found in these experiments to be toxic, yet other investigators have found it beneficial.⁷³ It would, however, be equally unsafe to draw the converse deduction and, because nutritive substances can produce toxic effects, assume that toxic substances can therefore exert growth-producing effects.

Plant Poisons.

The action is further complicated by the fact that two substances acting together may behave very differently from either acting separately.⁷⁴

Two practical problems arising out of toxicity have been dealt with this year.

(1) *Effect of Lead Compounds on Vegetation.*—Considerable trouble has been experienced in the past through the refuse from lead mines washed down on to agricultural land. J. J. Griffith⁷⁵ has made a careful study of the effects produced in Cardiganshire. Leguminous crops appear to suffer most, although all were affected, and in the case of root crops so much lead or zinc compound sometimes adhered to the roots as to cause injury to the animals eating them. A heavy dressing of lime afforded the best remedy.

⁷¹ H. G. Söderbaum, *Kongl. Landbruks-Akad. Handlingar*, 1917, **56**, 537; *A.*, i, 60.

⁷² Compare G. Ciamician and C. Ravenna, *Atti R. Accad. Lincei*, 1919, [v], **28**, i, 13; *A.*, i, 241. For an investigation into the effect of poisonous organic substances on germination and seedling growth, see I. Traube and H. Rosenstein, *Biochem. Zeitsch.*, 1919, **95**, 85; *A.*, i, 509.

⁷³ L. Hiltner and M. Kronberger, *Chem. Zentr.*, 1919, **90**, i, 1039.

⁷⁴ Compare W. E. Totttingham and A. J. Beck, *Plant World*, **19**, 359; *A.*, i, 510.

⁷⁵ *J. Agric. Sci.*, 1919, **9**, 366.

(2) *The Poisonous Effects of Coal Gas on Plants*.—It is shown that the toxicity is a positive effect, and is not due to displacement of oxygen, but is associated with the constituent to which the characteristic odour of coal gas is due. When this is removed, the toxicity ceases.⁷⁶ Subsequent experiments⁷⁷ indicated hydrocyanic acid as the most probable agent.

The Composition of Plants and the Changes during Growth.

The composition of the plant taken as a whole alters continuously during the entire period of growth, but the change appears to be on definite lines. For this particular purpose the plant may be regarded as made up of two parts, namely, the framework and the contained material. Each of these is tolerably constant in composition for a given plant, the variations being within fairly definite limits, but the relative proportions of framework and contained material vary considerably, although quite regularly, at different periods of plant growth.

The process of ripening and seed formation then consists in the transfer of the cell contents (or a part thereof) to the seed heads.

Certain plants—wheat, mangolds—have in the past been studied in some detail at Rothamsted, and the conclusion has been drawn that whatever the circumstances, so long as the plant grows at all, it will continue to make material of the same general character, and to send this into the framework or the seed heads. During the present year, the course of the growth processes in the sorghum plant has been studied in the United States,⁷⁸ and the results indicate that the plant during the earlier part of the season builds up its cellular structure of fibre, protein, and mineral material, whilst in the later stage it fills up these tissues with carbohydrates—starch in the seed and sugar in the stalk. No evidence was found that the leaves are deprived of carbohydrates to supply the stalk. Maturation of the seed heads consists almost entirely in the filling out of a fibre and protein framework with starch.

All the plant constituents, whatever their nature, are derived in the plant from the sugar produced by photosynthesis, and the nitrates, phosphates, and other inorganic substances taken up by the roots. Little is known of the mechanism of the changes involved, and there is still much to be learnt of chemical constitu-

⁷⁶ C. Wehmer, *Ber. Deut. bot. Ges.*, 1918, **36**, 140; *A.*, i, 114.

⁷⁷ C. Wehmer, *ibid.*, 460; *A.*, i, 304.

⁷⁸ J. J. Williams, B. M. West, D. O. Sprietstersbach, and G. E. Holm, *J. Agric. Res.*, 1919, **18**, 1.

tion of the substances themselves. Light is certainly essential, and the different wave-lengths have different effective values.⁷⁹

It has been supposed, and possibly correctly, that formaldehyde is the first product of photosynthesis, but the evidence is rendered incomplete by the circumstance that formaldehyde may perhaps arise from the decomposition of chlorophyll.⁸⁰

The first substance detectable with certainty in the chain of photosynthesis is sucrose, which is subsequently hydrolysed to dextrose and lævulose. The next stages, however, are involved in considerable obscurity. It has been urged that the dextrose is used up to form cell contents or for purposes of respiration, whilst the lævulose is used for making the framework. Unfortunately, the amount of lævulose cannot be estimated with any degree of accuracy,⁸¹ so that its movements cannot be followed. It has, indeed, been claimed this year that the ratio dextrose/lævulose can be determined; it is claimed, also, that this ratio is less than unity in the parenchyma of the leaf, but increases in the stem.⁸² If this were true, it would be consistent with the view that dextrose alone is used up for respiration, since respiration is greater in the leaf than in the stem. It does not appear, however, that the objections of Davis to the analytical process have really been met. Notwithstanding the unsatisfactory nature of the evidence, however, it is still permissible to think of the lævulose as being concerned mainly in building framework and the dextrose mainly in providing material for cell contents and respiration.

Little has been added this year to our knowledge of the framework. A paper has appeared⁸³ on the furfuroids (related to cellulose) of sugar beet, but it is mainly of analytical interest; it deals also with the pectoses, the supposed cementing material binding the framework together. An attempt has been made to ascertain whether the marked effect of potassium fertiliser on grass and cereal stems is due to any stiffening of the framework. Microscopic examination, however, failed to reveal any difference in structure;⁸⁴ the effect is presumably to be attributed to differences in turgidity.

Much more work has been done on the cell contents. The dextrose generated from sucrose is not usually stored as such, but is generally converted into starch. This, however, does not remain as starch, but is again hydrolysed, and may again be regenerated

⁷⁹ A. Ursprung, *Ber. Deut. bot. Ges.*, 1918, **36**, 73, 86; *A.*, i, 112.

⁸⁰ W. J. V. Osterhout, *Amer. J. Bot.*, 1918, **5**, 511; *A.*, i, 597.

⁸¹ W. A. Davis, *J. Agric. Sci.*, 1916, **7**, 327.

⁸² H. Colin, *Compt. rend.*, 1919, **168**, 697; *A.*, i, 241.

⁸³ R. Gillet, *Bull. Assoc. Chém. Sucr.*, 1918, **35**, 93; *A.*, ii, 302.

⁸⁴ O. N. Purvis, *J. Agric. Sci.*, 1919, **9**, 338.

either from dextrose or from some of the other substances produced in the cell. A considerable number of sugars appear to be capable of conversion into starch in at least certain plant cells; thus, *Spirogyra* in water free from carbon dioxide can form starch from dextrose, lævulose, galactose, raffinose, methyl alcohol, glycerol, or ethyl acetate in the presence of dipotassium hydrogen phosphate and formaldehyde. It does not, however, form starch under these conditions from lævulose, sorbose, arabinose, xylose, rhamnose, and other substances.⁸⁵ *Aspergillus* has similar wide powers of producing starch under certain conditions.⁸⁶ Of course, these substances are not necessarily all found in the plant cell, but some of them are widespread; carrots have been shown to contain mannitol and dextrose, whilst green peas contain mannitol, dextrose, lævulose, and glycuronic acid.⁸⁷ Moreover, starch is not always found; in some cases, the product is inulin or the very similar inulinin.⁸⁸ The carbohydrate occurring in lichens has also been studied,⁸⁹ chiefly, however, with the view of obtaining a fermentable sugar. The gums of the sorghum plant have been found to consist of complexes of galactose and pentosans with about 20 per cent. of mineral matter, chiefly calcium, magnesium, and potassium.⁹⁰

Some of the plant constituents are simpler in composition than the sugars, and may be regarded either as degradation products of dextrose or lævulose, or as accompanying products in the synthesis of sucrose. One of the commonest is oxalic acid. A suggested improvement in the method of identifying this substance in plants consists in substituting ferrous ammonium sulphate⁹¹ for the potassium salts now often used. For the purpose of localising the oxalates, a highly concentrated solution of the ferrous salt is injected into the plant by means of an air pump, when precipitation of the ferrous oxalate occurs within the cell in which the acid occurs. Other methods suggested have involved precipitation with saturated alcoholic sodium or potassium hydroxides, lead acetate, and barium chloride.⁹²

The presence of a salt of aconitic acid in the juice of the sugarcane seems to be established.⁹³ The sorghum plant also contains

⁸⁵ T. Bokorny, *Biol. Zentr.*, 1916, **36**, 385; *A.*, 1918, i, 366.

⁸⁶ F. Boas, *Ber. Deut. bot. Ges.*, 1919, **37**, 50; *A.*, i, 508.

⁸⁷ E. Busolt, *J. Landw.*, 1916, **64**, 357, 361; *A.*, i, 564.

⁸⁸ E. Cuvreur, *Compt. rend. Soc. biol.*, 1918, **81**, 40; *A.*, 1918, i, 366.

⁸⁹ E. Salkowski, *Zeitsch. physiol. Chem.*, 1919, **104**, 105; *A.*, i, 242.

⁹⁰ J. J. Williams, R. M. West, D. O. Sprietstersbach, and G. E. Holm, *J. Agric. Res.*, 1919, **18**, 1.

⁹¹ N. Patschovsky, *Ber. Deut. bot. Ges.*, 1918, **36**, 542; *A.*, i, 303.

⁹² H. Molisch, *Flora*, 1918, **11-12**, 60; *A.*, i, 191.

⁹³ C. S. Taylor, *T.*, 1919, **115**, 886.

aconitic acid in addition to malic, citric, tartaric, and oxalic acids.⁹⁴

On the other hand, the simplest of all organic acids, formic acid, is of rare occurrence; its presence has been demonstrated in the hairs of stinging nettles,⁹⁵ but it is not usual elsewhere.*

The organic phosphorus reserve compound of plants has been studied in some detail in France, and its identity apparently established. In the first place, crystalline salts were isolated, which on analysis gave the formula $C_6H_{12}O_{27}P_6Na_{12}$ (or Na_3Ca_2), $44H_2O$.⁹⁶ Further investigation showed that three molecules of water were so strongly retained that they could not be removed except by decomposing the compound; the formula was then altered to $C_6H_6O_{24}P_6Na_{12}$, $47H_2O$.⁹⁷ This indicated a hexose hexaphosphate, and examination showed the substance was really an inositol hexaphosphate. The evidence was clinched by synthesising inositol hexaphosphate by heating inositol with phosphoric acid in the presence of phosphoric oxide at 120–130° for three hours, and then showing that the double sodium calcium salt had identical crystallographic properties with that prepared from the naturally occurring substance.⁹⁸

Besides the sugars and the phosphorus compounds, there are large numbers of other plant constituents, some of which are chemically simple and others are not. There is a steady increase in chemical knowledge of the complex plant substances. Fortunately, the investigations of Willstätter on chlorophyll are continuing.⁹⁹

Another group of constituents at least as complex as chlorophyll are the chromatins. Investigation of these substances is difficult, and little has been added to our knowledge during the year. It is now stated that the substance previously described by Dangeard as metachromatin in higher plants is not comparable with the metachromatin of fungi, but is a phenolic compound capable of being converted into anthocyanin.¹ A large body of constituents is,

⁹⁴ J. J. Williams, R. M. West, D. O. Sprietstersbach, and G. E. Holm, *J. Agric. Res.*, 1919, **18**, 1.

⁹⁵ L. Dobbin, *Proc. Roy. Soc. Edin.*, 1918–19, **39**, 137; *A.*, i, 614.

⁹⁶ S. Posternak, *Compt. rend.*, 1919, **168**, 1216; *A.*, i, 426.

⁹⁷ S. Posternak, *ibid.*, **169**, 37; *A.*, i, 426; Society of Chemical Industry in Basle, *Brit. Pat.* 130456; *A.*, i, 504.

⁹⁸ S. Posternak, *ibid.*, 138; *A.*, i, 433.

⁹⁹ R. Willstätter, O. Schuppli, and E. W. Mayer, *Annalen*, 1919, **418**, 121; *A.*, i, 448.

For a discussion of the bearing of this work on the mechanism of assimilation see R. Willstätter and A. Stoll (*Ber.*, 1917, **50**, 1777; *A.*, 1918, i, 207) and K. Schaum (*Ber.*, 1918, **51**, 1372; *A.*, i, 111).

¹ A. Guilliermond, *Compt. rend.*, 1918, **166**, 958; *A.*, 1918, i, 366.

however, proving more amenable to chemical treatment. The tannins, which are very widely spread, have been studied by Emil Fischer,² and their relation to the mellowing of fruits has been discussed by C. Griebel and A. Schäfer.³

Some new or little known glucosides have also been described, some occurring in the cotton plant⁴ and some in the orchid.⁵ The saponin occurring in lucerne has also been studied; its formula is given as $C_{27}H_{37}O_{16}N$; it is abnormal in that it contains nitrogen and does not hæmolyse blood. Like other saponins, it poisons fish, but it is said to act by preventing the diffusion of air into the water, and not in virtue of any special toxic property.⁶ Other saponins investigated have been from the root of *Platycodon grandiflorum*.⁷

The substance indican is of special interest, because of its great technical importance in connexion with indigo. Davis claims that there is a marked need for phosphatic fertilisers in order to secure a proper yield under Indian conditions.⁸ A new method of preparing indican from the indigo plant has also been described, and is said to be more rapid and complete than other methods.⁹

From the agricultural point of view, the nitrogen compounds are often more interesting than the others. It has been customary to identify these by hydrolysis with hydrochloric acid and examination of the products by the Van Slyke method. Whilst the method has advantages, there is considerable evidence that it breaks down in particular cases.¹⁰

The only safe plan is to isolate the protein and study it in as pure a state as possible. It is known that the protein is formed in some way from sugar and an inorganic nitrate, and an attempt¹¹ has been made to express the course of the reaction. It is assumed that the sugar reacts with nitrogen, phosphorus, and sulphur derived from inorganic salts to yield proteins; the bases of the salts

² E. Fischer and M. Bergmann, *Ber.*, 1918, **51**, 1760; 1919, **52**, [B], 829; *A.*, i, 87, 278.

³ *Zeitsch. Nahr.-Genussm.*, 1919, **37**, 97; *A.*, i, 427.

⁴ A. Viehoveer, L. H. Chernoff, and C. O. Johrs, *J. Agric. Res.*, 1918, **13**, 345; *A.*, 1918, i, 367. Also E. E. Stanford and A. Viehoveer, *ibid.*, **13**, 419; *A.*, 1918, i, 367.

⁵ E. Bourquelot and M. Bridel, *Compt. rend.*, 1919, **168**, 701; *A.*, i, 243.

⁶ G. A. Jacobson, *J. Amer. Chem. Soc.*, 1919, **41**, 640; *A.*, i, 375.

⁷ H. Oshika, *Kyoto Igaku Zasshi*, 1918, **15**, 76; *A.*, i, 427.

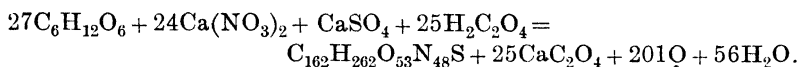
⁸ *Agric. J. India*, 1919, **14**, 21.

⁹ B. M. Amin, *Agric. Res. Inst. Pusa, Indigo Publ.*, No. 5; *A.*, i, 283.

¹⁰ J. F. Brewster and C. L. Alsberg, *J. Biol. Chem.*, 1919, **37**, 367; *A.*, i, 239.

¹¹ A. Meyer, *Ber. Deut. bot. Ges.*, 1918, **36**, 508; *A.*, i, 240.

are thereby liberated and neutralised by the organic acid produced in the leaves; the process is formulated thus:



The interest of the agricultural chemist in the constituents of plants lies in their feeding value to men and animals but especially animals, and this depends on two types of compounds, the nutrients, of which large quantities are required, and the vitamins, needed only in small amounts. Water-soluble vitamins have been found in the bulb of the onion, the root of the turnip,¹² the fruit of the tomato, and the leaves, stem, and root of the beet. In the case of clover, lucerne, and timothy, the larger amount of vitamins was found in the immature plant, which may help to account for the superior feeding value of the younger over the older grass.

The antiscorbutic factor present in green peas is lost on drying, and hence dried peas and lentils are not as valuable in a dietary as they might be. H. Chick and E. M. Delf have shown,¹³ however, that the factor increases five or six times in amount when the peas are soaked for twenty-four hours and then allowed to germinate for forty-eight hours; the amount then becomes equal to that found in green peas and potatoes, and greater than that in carrots or beetroots.

In the case of wheat grain, the water-soluble vitamins appear to be localised in the endosperm, but it is not uniformly distributed there. None could be found in the pure embryo.¹⁴

The nutritive value of the constituents is more properly dealt with by the physiologist than the agriculturist. Reference may be made, however, to the extensive paper, just quoted, by Osborne and Mendel on the nutritive value of the wheat kernel and its milling products.

The Mechanism of the Reactions in the Plant.

Although very little is known of the course of the reactions in the plant, some knowledge has been gained of the conditions determining them.

In the first place, the so-called mineral elements—potassium, calcium, phosphorus, etc.—are essential, although this fact is often overlooked in attempts at reconstructing the plant processes.

¹² T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, 1919, **39**, 29; *A.*, i, 510.

¹³ *Biochem. J.*, 1919, **13**, 199.

¹⁴ T. B. Osborne and L. B. Mendel, *J. Biol. Chem.*, 1919, **37**, 557; *A.*, i, 298.

Analyses of the plant ash are frequently made,¹⁵ and, whilst the figures are not at present illuminating, they will presumably some day find an interpretation. One instance only need be quoted, the case of the ash of the spinach plant grown under conditions of high manuring.¹⁶ The constituents fall into two groups: those present in quantity but varying little, whatever the fertilisers added to the soil—lime, magnesia, manganese, alumina, iron, phosphorus, and sulphur—and those that show great fluctuations in the quantity present, including silica, potash, and soda. The variations sometimes, but not always, are in the same direction as those in the soil.

The ash constituents sometimes precipitate out as the result of interactions in the plant.

The second important consideration is that the processes are carried on in the main by enzymes. A little reflection will show that this is necessary, since the ordinary means of expediting a reaction by rise of temperature or of concentration are inapplicable in the growing plant; a catalyst is therefore essential.

A discussion of the enzymes of plants would be outside the scope of this Report; it is possible only to indicate some of the work carried out during the year. Undoubtedly the paper of most general interest is one describing an attempt by Willstätter and Stoll to work out the constitution of peroxylase, using the material obtained from the horse radish. They endeavoured to prepare pure specimens of the enzyme so as to find out whether it is a single substance or a system of co-operating substances, whether a metal is an integral part of the enzyme, and what atomic groups are responsible for enzymic activity.¹⁸ The enzyme does not appear to be hopelessly complex in structure; it seems to consist chiefly of a nitrogenous glucoside containing a pentose and a molecular quantity of another sugar, probably a hexose. Mineral matter is also present, but iron, at any rate, scarcely seems necessary for the effective action of the enzyme.

Other papers of interest include one on the oxydases of sugar-

¹⁵ See, for example, L. Leroux and D. Leroux, *Ann. Chim. anal.*, 1919, [ii], 1, 207; A., i, 563; A. Lacroix, *Compt. rend.*, 1918, 166, 1013; A., 1918, i, 366.

¹⁶ R. H. True, O. F. Black, and J. W. Kelly, *J. Agric. Res.*, 1919, 16, 15. •

¹⁷ A. Wichmann, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 968; A., i, 564 (phosphates); also H. Molisch, *Ber. Deut. bot. Ges.*, 1918, 36, 277, 474; A., i, 113, 242 (silica).

¹⁸ R. Willstätter and A. Stoll, *Annalen*, 1918, 416, 21; A., 1918, i, 555.

cane,¹⁹ of the pear and the potato,²⁰ of seeds,²¹ and of fresh and dried vegetables.²²

An attempt has been made to express the degradation of starch under the action of diastase.²³

The vegetable proteases have also been investigated, and the proteinoclastic and peptoclastic action of leaves measured at different periods of growth.²⁴

One of the most characteristic reactions in the plant is the production of amino-acids by the interaction of sugar and nitrate. Presumably reduction takes place at some stage, and O. Baudisch²⁵ has attempted to reproduce the reaction in the laboratory; he has worked out a reduction which resembles the natural process in that an iron salt and oxygen both take part. B. Moore has also investigated the early stages in the synthesis of nitrogen compounds.²⁶

Feeding Stuffs.

Several investigations have been made on the feeding value to animals of green crops. Green maize has been studied to find out the cause of the loss of sugar which is known to occur soon after the plant is cut. It is suggested²⁷ that this loss is only in part due to respiration; most of it is attributed to condensation to form more complex substances, especially starch. It is known that the sugar content of green sweet maize falls off rapidly when the plant is cut.

Certain green crops occasionally have harmful, and even fatal, effects on cattle. C. T. Dowell²⁸ records a case in Oklahoma where sorghum cut when 75 cm. high, at a time of great drought, killed no fewer than ten out of twelve cattle within an hour. Investigation showed this to be a case of cyanogenesis. It was shown, however, that dried sorghum and mature sorghum are both safe feeding stuffs; if in a less mature sample there is any doubt about the presence of the cyanogenetic glucoside, the ill-effects can be obviated by giving some concentrated feeding stuffs. The explanation sug-

¹⁹ R. Narain, *Agric. J. India*, 1918, 47; *A.*, i, 114.

²⁰ M. W. Onslow, *Biochem. J.*, 1919, 13, 1; *A.*, i, 361.

²¹ W. Crocker and G. T. Harrington, *J. Agric. Res.*, 1918, 15, 137; *A.*, i, 110.

²² K. G. Falk, G. McGuire, and E. Blount, *J. Biol. Chem.*, 1919, 38, 229; *A.*, i, 426.

²³ M. Samec, *Koll. Chem. Beihefte*, 1919, 10, 289; *A.*, i, 472.

²⁴ E. A. Fisher, *Biochem. J.*, 1919, 13, 124; *A.*, i, 464.

²⁵ *Ber.*, 1919, 52, [B], 35, 40; *A.*, i, 237, 238.

²⁶ *Proc. Roy. Soc.*, 1918, [B], 90, 158; *A.*, 1918, i, 365.

²⁷ C. O. Appleman and J. M. Artt, *J. Agric. Res.*, 1919, 17, 137.

²⁸ *Ibid.*, 16, 175.

gested is that the dextrose and maltose produced by salivary digestion prevent liberation of the hydrocyanic acid.

A common method of preserving green food over the winter is to cut it up and store it under anaerobic conditions in a large vat called a silo; the product is known as silage. The sugars rapidly change to acetic and other fatty acids, and a certain amount of hydrolysis of the proteins takes place, but after the first rapid reactions there is little subsequent change, and the material keeps all through the winter. More products are periodically found in the silage; this year, acetylmethylcarbinol has been detected in sorghum silage.²⁹ Analyses have been made of the mixture occurring in ensiled cabbage, or sauerkraut.³⁰

Agricultural chemists have long tried to solve the problem of evaluating the fibre in feeding stuffs, the conventional method of successive acid and alkali treatment suffering from certain disadvantages; in particular, it dissolves some material which the animal cannot digest. A new method, based on the absorption of chlorine by the fibre, is claimed to give satisfactory results.³¹

Another analytical problem as yet unsolved is to discriminate between one nitrogen compound and another in a feeding stuff. The Van Slyke method has obvious advantages, although, as already pointed out, it is liable to fail in dealing with plant products. Two improvements have been effected³²: (1) preliminary extraction, first with ether and then with cold absolute alcohol, to remove non-protein substances that interfere with the reaction, and (2) reduction in the amount of humin nitrogen formed during the reaction. It is claimed that these improvements put the method on a much more satisfactory basis.

The hydrogen electrode has been used for determining the acidity and the titratable nitrogen in wheat. The process is not quite simple, as the substances in the solution formed when wheat is extracted with water are not ionised until an alkali has been added.³³

²⁹ W. G. Friedemann and C. T. Dowell, *J. Ind. Eng. Chem.*, 1919, **11**, 129; *A.*, i, 244.

³⁰ V. E. Nelson and A. J. Beck, *J. Amer. Chem. Soc.*, 1918, **40**, 1001; *A.*, 1918, i, 364.

³¹ P. Waentig and W. Gierisch, *Zeitsch. physiol. Chem.*, 1918, **103**, 87; *A.*, ii, 173.

³² H. C. Eckstein and H. S. Grindley, *J. Biol. Chem.*, 1919, **37**, 373; *A.*, ii, 204.

³³ C. O. Swanson and E. L. Tague, *J. Agric. Res.*, 1919, **16**, 1; *A.*, ii, 176.

Insecticides and Fungicides.

Investigation has been made into the composition of Burgundy mixture,³⁴ a well-known and very useful copper spray, and of the sulphur washes.³⁵ In addition, there has been some work on the use of formaldehyde vapour for seed disinfection,³⁶ and of chlorpicrin³⁷ for the killing of insects. The investigation of the changes in composition undergone by arsenical fluids in cattle-dipping baths has led H. H. Green in South Africa to the interesting discovery of certain bacteria capable of oxidising arsenites to arsenates, and of others capable of reducing arsenates to arsenites.³⁸

E. J. RUSSELL.

³⁴ R. L. Mond and C. Heberlein, *T.*, 1919, **115**, 908.

³⁵ J. V. Eyre, E. S. Salmon, and L. K. Wormald, *J. Agric. Sci.*, 1919, **9**, 283.

³⁶ C. C. Thomas, *J. Agric. Res.*, 1919, **17**, 33.

³⁷ G. Bertrand, Brocq-Rousseu, and Dassonville, *Compt. rend.*, 1919, **169**, 1059, 1428.

³⁸ *Union of S. Africa, 5th and 6th Reports, Veterinary Research*, 1919, 593.

CRYSTALLOGRAPHY.¹

THREE important advances are to be noted in the province of X-ray investigation, so far as concerns this Report. The first is the independent and almost simultaneous development, by Debye and Scherrer in Germany and Hull in America, of an ingenious method of investigating crystal aggregates; this method was just mentioned in a previous Report, but requires further notice now that the original literature is available.

The nature of the second advance can best be described by a quotation from Hull's paper on the structure of iron.² "It is very difficult to conceive of any arrangement of point atoms which will [account for the experimental data]. We are forced, I think, to look for the explanation in the internal structure of the atoms. If it is assumed that all the twenty-six electrons . . . are displaced from the centre of the atom along the cube diagonals in four groups of 2, 8, 8, 8 at distances $1/32$, $1/16$, $1/8$, and $1/4$ respectively of the distance to the nearest atom, all the observed facts are accounted for within the limits of experimental error." It may be added that the same degree of penetration is characteristic of Debye and Scherrer, who believe they have proved that salts are ionised in the crystalline state.

The third advance relates to the application of X-ray methods to the study of amorphous substances, including colloids. Debye and Scherrer have shown that charcoal is really crystalline, and Scherrer³ has proved that colloidal particles of silver and gold, as also gels of silicic and stannic acids, are in reality ultramicroscopic crystals. Apparently the only substances which may be neglected

¹ The Reporter regrets that owing to lack of space the consideration of some important mineralogical researches has had to be postponed. It is hoped to treat these adequately in the 1920 Report. Miss M. W. Porter has kindly drawn some of the figures, and Mr. R. C. Spiller has assisted greatly in the preparation of the manuscript, and the writer would take this opportunity of thanking them for their kind co-operation.

² A. W. Hull, *Physical Rev.*, 1917, [ii], 9, 84.

³ P. Scherrer, *Nachr. Ges. Wiss. Göttingen*, 1918, 96; A., ii, 274.

by the crystallographer are glass, and such organic materials as celluloid, collodion, gelatin, albumin, cellulose, and starch.

X-Ray methods of exploring crystal structure appear to have reached a definite stage of development, so that a general appreciation may not be altogether devoid of interest. One matter of detail may be mentioned immediately. The face-centred lattice and its derivatives (the diamond "lattice," the blende and pyrites structures, and so on) no longer wholly represent the family of cubic structures, for there are now several examples of the cube-centred lattice.

The fifth and concluding volume of Groth's invaluable "Chemische Krystallographie" has appeared.

It has, of course, long been known that silver or copper is just as easily attacked by nitric acid as gold is resistant; also that an admixture of gold (erroneously believed to be 25 per cent.—"quar-tation") protects silver or copper from action. As a result of patient tests with more varied reagents, Tammann has proved the existence of reaction-limits, at such definite metal concentrations as are expressible by simple multiples of $1/8$. Apparently, there are several degrees of nobility in the silver-gold and copper-gold series of alloys, the investigation of which has not only told us much concerning the chemical properties of a space-lattice, but has also led to an interesting interpretation of a variety of properties, ranging from optical anomalies in mixed crystals to the temper of a metal.

Two commemorations have been celebrated. The first, in honour of the 175th anniversary of the birth of the Abbé Haüy, has been accompanied by the issue of a special number of the *American Mineralogist* containing many interesting portraits, facsimile letters, and some eight essays by American mineralogists. The centenary of the foundation of the *American Journal of Science* has also been worthily signalled by the appearance of a special number,⁴ containing historical accounts of the development of world science in general and of American science in particular. Apparently the first American Mineralogical Society was founded in 1799.

The gradual transformation undergone by the science of mineralogy during the last fifty years has been eloquently described in recent accounts by Sir H. A. Miers⁵ and G. T. Prior.⁶ The progress of crystallography is not less amazing. Crystal structure is becoming more and more a happy hunting ground for all kinds of physicists; and it seems not impossible that the complexities of the gaseous and fluid conditions (which appear to be relatively simple, since they are merely studied in the aggregate) will only be un-

⁴ "A Century of Science in America," *Amer. J. Sci.*, 1918, [iv], 46, 1.

⁵ *T.*, 1918, 113, 363.

⁶ *Geol. Mag.*, 1919, [vi], 6, 10.

ravelled when crystal structure shall have been profoundly elucidated.

X-Ray Methods of Exploring Crystal Structure. The Debye-Scherrer-Hull Method of X-Ray Exploration.

This ingenious method of studying crystal structure, when the material is an irregular aggregate of tiny crystals, not necessarily endowed with plane faces, was independently and almost simultaneously devised by Debye and Scherrer⁷ and Hull.⁸ Although formally the method is an extension of the original Laue photographic method, all interpretations have, of course, been really rendered feasible by the spectrometric researches of W. H. and W. L. Bragg. The following account was compiled in the first instance from Hull's

FIG. 1a.

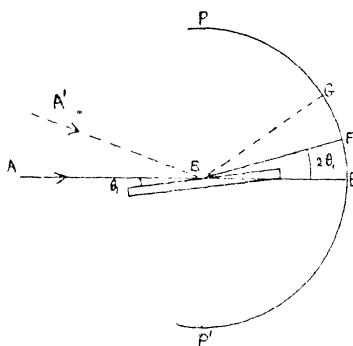
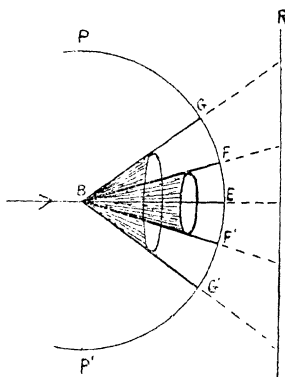


FIG. 1b.



paper because it was more accessible. It will be seen later that Debye-Scherrer and Hull only differ in subsidiary details.

Suppose (Fig. 1a) a monochromatic beam of X rays, AB (which has already passed a series of fine slits), be allowed to impinge on the cube face of a crystal of potassium chloride, at the correct glancing angle, θ_1 , for the first order "reflection," and the rays be received on a narrow photographic film, $P'EP'$, bent to the form of a semi-circle with centre B , then the film on development will show a much over-exposed line, E , due to the undeviated beam, and a line F , due to cumulative reflection, the distance of which from E is determined by the arc $2\theta_1$. If now the glancing angle be increased to a new value, θ_2 (the appropriate angle for the second order reflection), a

⁷ P. Debye and P. Scherrer, *Physikal. Zeitsch.*, 1916, **17**, 277; 1917, **18**, 291; *A.*, 1917, ii, 937.

⁸ A. W. Hull, *Physical Rev.*, 1917, [ii], **10**, 661.

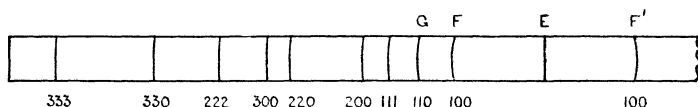
new line, G , will make its appearance, the arc EG being measured by $2\theta_2$; and so on for a third or still higher order.

In all cases the glancing angles of intense reflection are related to the distance, d_{100} , between successive structural planes, by the equations, $\lambda = 2d \cdot \sin \theta$, $2\lambda = 2d \cdot \sin \theta_2$, $3\lambda = 2d \cdot \sin \theta_3$, and so on.⁹

If, again, dodecahedral and octahedral plates be subject to experiments, new lines will appear, in positions involving the new grating distances d_{110} and d_{111} .

Now consider what will happen if some very finely powdered potassium chloride be placed at B (instead of a crystal plate) and an exposure taken without troubling about any particular glancing angle (Fig. 1*b*). There will simultaneously be a considerable number of minute crystals having the same orientation as the first crystal considered above, but these will only constitute the members of a larger group, making the same angle with the incident beam, but lying in all azimuths. The "reflected" beams from crystals of this group will form a hollow cone of total angle $4\theta_1$, and will intercept the film in symmetrical positions F and F' . There will be many

FIG. 2.



other crystals having the second kind of orientation, which will give rise to the hollow cone GBG' , and so on. (If a plane film, R , were used concentric circular impressions would result, but a plane film of manageable dimensions would only register cones up to 4θ , where $\theta = 22\frac{1}{2}^\circ$). After the semi-circular film has been unbent and developed, the lines on the portion EP for the first three order reflections will be in the positions given in Fig. 2, in which the indices (222) signify a second-order reflection from (111), and so on. It will be realised that the linear distance of any line from E is a simple function of (1) the radius of the bent film, (2) the wave-length of the X-rays used, (3) the order of the reflection, and (4) the fundamental grating distance, d , of the atomic strata, responsible for that line.

In the actual case of potassium chloride there would, of course, be more than nine lines. The number of lines is dependent on the wave-length of the monochromatic X-rays employed, for, although the number of possible structural planes is infinite, only those planes

⁹ The Reporter regrets the slip involved in a previous Report (*Ann. Report*, 1914, p. 240, lines 22-27).

can reflect any energy the distances apart of which are greater than $\lambda/2$. Thus, there is a limit to the number of lines, depending on both structure and wave-length employed. The following table refers to the diamond.

X-Rays used.	Wave-length.	No. of lines theoretically possible.
Tungsten doublet	0.212×10^{-8}	More than 100.
Rhodium doublet	0.617	30.
Molybdenum (K_{α} -doublet) ...	0.712	27.
Iron doublet	1.93	Only 3, namely, from $\{111\}$, $\{110\}$, $\{311\}$.

From the method of experimentation it will, perhaps, be obvious that a form $\{311\}$ of the diamond, consisting of twelve structural planes, will only give one line. The existence of the twelve planes merely enhances by twelve the chance that a crystal shall have the correct orientation; accordingly, the intensity of the line is proportionately increased. This property constitutes an advantage in the study of planes of the general indices $\{hkl\}$, for the co-operation of the twenty-four planes (of a cubic crystal), each of which will have a subordinate reflectivity, may lead, so to speak, to a combined creditable effort.

The principles and routine of the interpretation are clearly expounded by Hull and applied to the analysis of ten crystal aggregates, one of which, the diamond, was purposely selected as a check. In theory, nothing need be known about the system or "crystal elements," but, in practice, if these are known the burden of analysis is greatly lightened.

The crystal powder (0.005 gram, or, if necessity compels, one-tenth of that) is best contained in a thin-walled tube of 1 mm. diameter. The material of the tube must naturally be amorphous (glass, celluloid, or collodion). Perfect irregularity of the crystal grains is desirable for uniform results, and can be ensured by rotating the tube during the exposure.

In order to render the X-rays more monochromatic, Hull always passes them through a suitable screen, which absorbs stray wave-lengths. If molybdenum rays are used, the screen should be zirconium or a compound like zircon.¹⁰

In a later paper the author¹¹ shows that his method can be employed successfully as a method of chemical analysis (that is, identification of substances the characteristic lines of which are already known). For example, a specimen of "chemically pure" sodium fluoride was found to exhibit the characteristic lines, both of sodium fluoride and sodium hydrogen fluoride, NaHF_2 . It is also

¹⁰ A. W. Hull and (Miss) M. Rice, *ibid.*, 1916, [ii], 8, 326.

¹¹ A. W. Hull, *J. Amer. Chem. Soc.*, 1919, 41, 1168; A., ii, 470.

evident that a mixture of sodium fluoride and potassium chloride can be readily distinguished from a mixture of the same bulk composition of sodium chloride and potassium fluoride, for the molecular volumes (and therefore grating distances) of the four compounds are different.

Debye and Scherrer press the powder into the form of a rod, and, if necessary, give it a coating of collodion to prevent disintegration during the radiation. The photographic film they arrange in the form of a cylinder, with axis perpendicular to the incident beam. The various cones intersect the film in curves represented schematically in Figs. 3 and 4, the last-mentioned figure representing half the unbent film. Of course, the linear distances only need be measured along the symmetry trace *XY*.

FIG. 3.

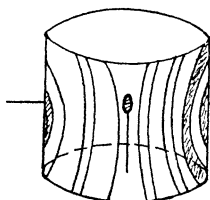
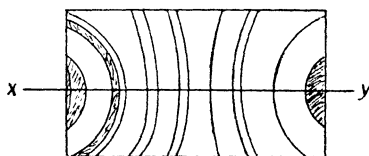


FIG. 4.



The method is absolutely trustworthy up to the point at which the interpretation begins. This point will be illustrated later under "graphite" (p. 203).

Recent Structure-Models.

The reconstructions or models offered by the various workers since the appearance of the last Report will now be considered. The list will be restricted to models which are relatively final, as space does not admit of any discussion of the less satisfactory cases. Grating distances are in all cases given in Ångström units, and must accordingly be considered as multiplied by 10^{-8} cm.

Cubic System.

"Cubic" lattice	None so far discovered.
Centred lattice.....	Tungsten (Debye*): $a = 3.18$ (length of cubelet edge).
	Iron (Hull); $a = 2.86$
	Sodium (Hull); $a = 4.30$.
	Lithium (Hull); $a = 3.50$ (author not entirely satisfied).

* P. Debye, *Physikal. Zeitsch.*, 1917, **18**, 483; *A.*, 1917. ii, 574.

Cubic System (continued).

Centred lattice	Nickel (Hull);	$a = 2.76$ { Hull believes to be dimorphous, but he is not sure).
Face-centred lattice ...	Nickel (Hull);	$a = 3.52$
	Aluminium (Hull);	$a = 4.05$.
	" (Scherrer*);	$a = 4.07$.
Diamond "lattice" ...	Diamond (Hull);	absolute agreement with W. H. and W. L. Bragg.
	Silicon (Debye and Scherrer†);	$a = 5.46$.
	" (Hull);	$a = 5.43$.
	Grey tin (the "tin-pest": Bijl and Kolkmeijer‡)	$a = 6.46$.
Rock-salt structure ...	Lithium fluoride (Debye and Scherrer§);	$a = 4.14$.
	Lithium fluoride, sodium fluoride, potassium fluoride, magnesia (Hull);	distances not stated.

* P. Scherrer, *Physikal. Zeitsch.*, 1918, **19**, 23; *A.*, 1918, ii, 113.

† P. Debye and P. Scherrer, *Physikal. Zeitsch.*, 1916, **17**, 277.

‡ A. J. Bijl and N. H. Kolkmeijer, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 501; *A.*, ii, 161.

§ P. Debye and P. Scherrer, *Physikal. Zeitsch.*, 1918, **19**, 474; *A.*, ii, 20.

|| A. W. Hull, *J. Amer. Chem. Soc.*, 1919, **41**, 1168; *A.*, ii, 470.

Hexagonal System.

Magnesium.—This interesting structure, unravelled by Hull, can be most simply described as Barlow's close-packed hexagonal system of spheres, slightly deformed. More precisely stated, there are two triangular, prismatic lattices¹² ($a = 3.22$, $c = 5.23$) so interposed that one centres the other.

Graphite.—This substance has been examined by Debye and Scherrer¹³ and by Hull,¹⁴ who suggest slightly different models. The former workers interpret the structure as an interpenetration of two face-centred rhombohedra (of edge 4.48), so that the vertex of one lattice lies one-third the full vertical distance (10.23) below the other. The vertical distances between successive horizontal layers of atoms is accordingly 3.41 (agreeing very well with W. H. Bragg's preliminary determination, 3.42); the crystallographic constant of the face-centred rhombohedral lattice, α , is $68^{\circ}26'$.

Hull's analysis takes the form of "an hexagonal structure, composed of four simple lattices of triangular prisms, each of side 2.47 and height 6.80, the atoms of the third lattice being directly above those of the first at a distance of one-half the height of the

¹² The term "triangular lattice" is a useful variant of "120°-prism lattice," for it obviates circumlocution in describing certain cases of interpenetration.

¹³ P. Debye and P. Scherrer, *Physikal. Zeitsch.*, 1917, **18**, 291; *A.*, 1917, ii, 437.

¹⁴ A. W. Hull, *Physical Rev.*, 1917, [ii], **10**, 661.

prism, those of the second and fourth lattices being above the centres of alternate triangles of the first, at distances $1/4$ and $8/14$ respectively of the height of the prism.¹⁵

A comparison of the above two models may well be given here, because the differences are so small as to make it improbable that the real solution will be agreed on before the lapse of several years. Debye and Scherrer used a copper anti-cathode and Hull one of molybdenum. This made it necessary to calculate all Debye and Scherrer's grating distances in order to eliminate inessentials due to different wave-lengths. The experimental results were then found to be in substantial agreement, both with regard to grating distances and intensities. Hull's reflections go far beyond the range of Debye and Scherrer's owing to the shorter wave-length of the molybdenum rays, and incidentally include a reflection, beyond Debye and Scherrer's observed lines, which will fit in with their unrepresented $(0\bar{2}2)$.¹⁵ On the other hand, Hull is not quite satisfied with his model because certain reflections are missing, the absence of which he refers to some special distribution or other of the electrons within the atom. The writer finds that all these reflections are represented in Debye and Scherrer's list of lines, with the possible exception of one line, which is attributed by them to the β -radiation of copper. If this line is in reality an α -line (the allocation of " α " or " β " appears to be sometimes a matter of opinion rather than exactness) all Hull's missing lines are accounted for, and presumably there need be no appeal to a special electronic distribution.

For simplicity of comparison Hull's refined estimates of level, $1/14$ and $8/14$, must be arbitrarily altered to $0/14$ and $7/14$ (without, of course, implying that his model is in any way incorrect). In each model atoms are then arranged in horizontal planes according to a bee-cell pattern. Moreover, the edge of the hexagon is the same within the errors of experiment, say, 1.45 . The bee-cell pattern will therefore be adopted as a medium of expression. The distances between successive layers is the same (3.40 — 3.42). The only difference is that Hull's third layer of bee-cells is vertically above the first layer, whilst in Debye and Scherrer's model every fourth layer is above the first. Plans of the two structures are given in Figs. 5 and 6, in which the various layers are distinguished by different kinds of lines and by the adoption of point-circles and circles of different radii for the atoms. Only two and three layers need be shown respectively in the two figures.

¹⁵ Debye and Scherrer's stated reflection $(0\bar{2}2)$ is really a first order reflection $(0\bar{1}1)$. Its absence would have seriously undermined their model—a point which they appear to have overlooked.

It is of interest to note that Debye and Scherrer regard the diamond as the prototype of aliphatic compounds (owing to the tetrahedral environment of each atom), and graphite as the prototype of aromatic compounds, since it can be held to illustrate three principal valencies in a horizontal plane and an unique valency, directed up or down, serving to interlock the various strata (compare, however, p. 208).

Charcoal.—"Amorphous" charcoal from most varied sources yields three lines, all of which are coincident with specific graphite lines. Debye and Scherrer have accordingly concluded that charcoal

FIG. 5.

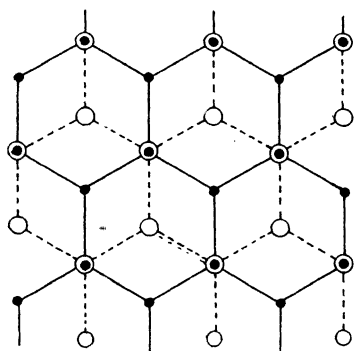
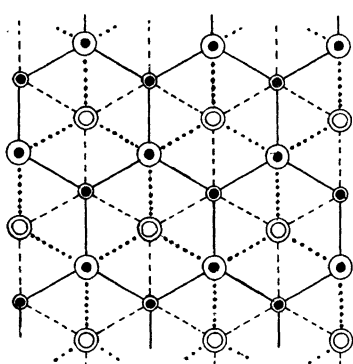


FIG. 6.



consists of polyatomic "molecules" (containing 20 or so atoms), these "molecules" being tiny fragments of the graphite structure.

Tetragonal System.

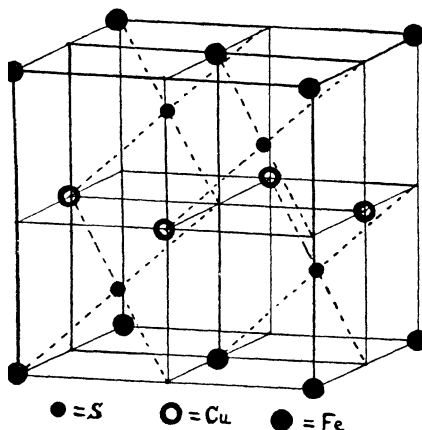
Chalcopyrite, CuFeS_2 .—This interesting mineral has been investigated by the Bragg method by C. L. Burdick and J. H. Ellis,¹⁶ who offer the model shown in Fig. 7, in which the copper and iron atoms taken collectively form what may be loosely described as a face-centred cubic lattice (the axial ratio $c:a=0.985$). The sulphur atoms are found to occupy the centres of half the smaller "cubes," selected tetrahedrally. The calculated intensities of the various reflections fit in very well with the observed values. A cursory glance at the figure will show that the structure is that of zinc blende, in which half the zinc atoms are replaced by copper atoms and half by iron atoms. Yet in spite of this great similarity zinc blende has a perfect dodecahedral cleavage, whilst chalcopyrite has none; moreover, an octahedral cleavage is characteristic of the

¹⁶ *J. Amer. Chem. Soc.*, 1917, **39**, 2518; *A.*, 1918, ii, 46.

related diamond structure. The property of cleavage is evidently as mysterious as the development of plane faces on a crystal. The Reporter finds the structure to be an example of the Fedorov point system 33s (Schönflies, V_d^3 ; Barlow, $59\beta_1$; Hilton, D_{3d}^3).

White Tin.—As in the case of the grey modification, the examination¹⁷ was carried out by means of the Debye-Scherrer method, and led to the result that a structural tetragonal cell (with dimensions $a=5.84$ and $c=2.37$) has its vertical sides centred; that is, there are three interpenetrating tetragonal lattices. Now the structure demands a value for the ratio $c:a=0.406$, which incidentally involves that the only common form, $p\{111\}$, should have the indices $\{403\}$. This perversion of form development is unexampled.

FIG. 7.



If the accuracy of the analysis is unquestionable, it signifies that little is definitely known about the correlation of form and structure.

Rhombohedral System.

Carborundum, CSi.—A thorough examination¹⁸ of this substance results in the following interpretation. The crystal is pseudo-cubic for the angle $\alpha=89^\circ56'$. The silicon and carbon atoms each furnish a "face-centred rhombohedral lattice,"¹⁹ the two lattices interpen-

¹⁷ A. J. Bijl and N. H. Kolkmeijer, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 494; *A.*, ii, 161.

¹⁸ C. L. Burdick and E. A. Owen, *J. Amer. Chem. Soc.*, 1918, **40**, 1749; *A.*, ii, 62.

¹⁹ It is, perhaps, worth while pointing out that the term "face-centred rhombohedral lattice" used by X-ray workers is one of convenience, and does not imply the existence of more than one Bravais lattice in the rhombo-

trating with a common vertical axis and in such a way that a horizontal layer of carbon atoms is displaced vertically through $0.36d$, where d signifies the distance between successive horizontal layers of carbon or of silicon atoms.

Addenda.—The model offered by Vegard and Schjelderup²⁰ for the alum group has been refuted by Niggli,²¹ who in turn offers a model, which cannot be considered for reasons of time and space. Several theoretical papers require a brief notice. The interpretation of the results of the Debye-Scherrer-Hull method is also discussed mathematically by C. Runge²² and by A. Johnsen and O. Toeplitz.²³ General explanatory papers and books on the relationship of X-ray work to the theory of crystal structure are becoming more numerous. The excellence of Kreutz's²⁴ book is only marred by the fact that he practically ignores the Fedorov-Schönflies point systems. Voigt²⁵ in an interesting paper is inclined to weigh the relative merits of Sohncke and Fedorov-Schönflies. It does not seem to be generally recognised that there is no question of a comparison of the Sohncke theory or of a somewhat halting, because *ad-hoc*-extended, later Sohncke theory with the Fedorov-Schönflies theory of the rhombohedral system. Any rhombohedral lattice can be described either as rhombohedral or as a centred-rhombohedral or as a face-centred rhombohedral lattice, each variant implying a specific axial ratio or fundamental angular constant α . Any particular choice is one of taste, in just the same way as is the allocation of the indices $\{110\}$ or $\{100\}$ or $\{\bar{1}11\}$ to, say, the cleavage, rhombohedron of calcite. It is interesting to note that, if the allocation of indices were consequential instead of conventional, the X-ray exploration of calcite demands the indices $\{100\}$ for the steep rhombohedron $f\{\bar{1}11\}$. The latter transformation was indeed suggested long ago by Goldschmidt, proceeding from what is really a principle of simplicity of indices which was subsequently developed by Fedorov and then abandoned because it was not sufficiently exact for the purposes of crystallo-chemical analysis. Even more radical transformations of indices have been advocated by Fedorov. It seems to the writer, however, that transformations are never expedient in conventional descriptions of crystal morphology, for they are liable to create confusion. On the other hand, in the practice of crystallo-chemical analysis all questions of taste or opinion have naturally to be rigorously subordinated to uniform principles, covering both the deduction of the space-lattice and the erection and orientation of that lattice. The tendency of Fedorov's and Goldschmidt's highly original work is to create barriers between the "old" and the "new" crystallography. These barriers are really built up of inessentials; their eventual removal will presumably lead to a fusion of the more reasonable elements of the conservative and progressive sections of crystallographers.

²⁰ L. Vegard and H. Schjelderup, *Ann. Physik*, 1917, [ii], 54, 146; *A.*, 1918, ii, 156.

²¹ P. Niggli, *Physikal. Zeitsch.*, 1918, 19, 225; *A.*, 1918, ii, 315.

²² *Ibid.*, 1917, 18, 509.

²³ *Ibid.*, 1918, 19, 47.

²⁴ S. Kreutz, "Elemente der Theorie der Krystallstruktur" (1915).

²⁵ W. Voigt, *Physikal. Zeitsch.*, 1918, 19, 237.

—however generally it is conceded in other branches of geometry that the whole necessarily includes the part.

Debye and Scherrer on Atomic Structure in a Crystal.

A recent paper by Debye and Scherrer²⁶ may, perhaps, be regarded as the present high-water mark of X-ray investigation. The authors advance certain theoretical considerations which serve to harmonise Braggs' principle (that the amplitude of reflected X-rays is proportional to the atomic weight) and Barkla's conclusion that the atomic weight is proportional to the intensity (square of the amplitude),²⁷ and they conclude that the intensity of radiation depends on the number (Moseley number) and posi-

FIG. 8.

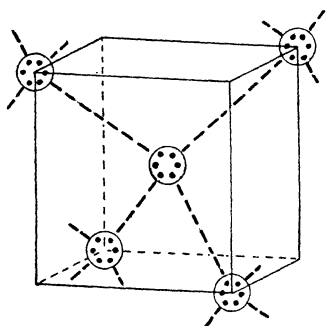
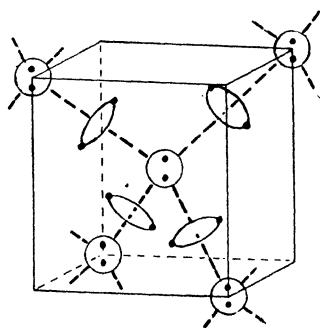


FIG. 9.



tion of the electrons in the atom. The authors believe that their method of X-ray experimentation is delicate enough to examine two questions of the greatest import.

The first of these questions relates to the mechanism of the attachment between atoms in a crystallised *element*. For example, in the diamond structure each carbon atom is environed tetrahedrally by four carbon atoms. Are the four atoms held by what may be termed chemical valencies? Now the chemical valency between the two atoms of a hydrogen molecule is at present interpreted mechanically as due to a midway dielectronic ring with a plane of rotation perpendicular to the valency bond. If this were also true for the diamond structure, the crystal would have the diagrammatic structure represented by Fig. 9, in which only two out of the six Moseley electrons of each carbon remain

²⁶ P. Debye and P. Scherrer, *Physikal. Zeitsch.*, 1918, **19**, 474; *A.*, ii, 20.

²⁷ W. H. and W. L. Bragg, "X-Rays and Crystal Structure," p. 49.

in the atom, and each of the other four, joined by one more from one of the four nearest atoms, rotates round a point which is located half-way between a pair of atomic centres. The differences between the new and the original Bragg structure (Fig. 8) are sufficiently great as to allow of a definite decision one way or the other, by means of a careful analysis of the intensities of the curves in a Debye-Scherrer X-radiogram. Amongst other things, there should be a strong second-order reflection from the octahedral planes. The result decisively negatives the subsistence of chemical valencies due to electronic rings and substantiates anew the Bragg structure. Moreover, other examples (of elements? not specified) have been investigated, and the authors have not been able to find a single case in which electronic rings serve as bonds in a crystal.

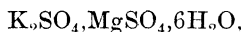
The second question relates to the possibility of ionisation in crystals of electrolytes. Since the reflecting power of an atom depends on the number of electrons, the power will be correspondingly modified by the loss or gain of an electron due to ionisation. As a result of a careful analysis of the X-radiogram of lithium fluoride (co-structural with the sodium chloride group), Debye and Scherrer conclude that the lithium has lost and the fluorine gained a negative electron. The method of reasoning is as follows. It is again assumed that the diffracting power of an atom is equal to the number of negative electrons as given by the Moseley number, namely, $\text{Li}=3$, $\text{F}=9$. In all the structural planes of lithium fluoride having three odd indices, for example, $\{111\}$, $\{113\}$, $\{133\}$, planes are alternately wholly lithium and wholly fluorine; the effective reflecting values will either be 2 and 10 or 3 and 9, accordingly as the structure is ionised or not. The authors conclude that the crystal is ionised.²⁸

General Conclusions: A Suggestion.

It has now become fairly evident that the X-ray method of exploring crystal structure is really a "sub-chemical" method.

²⁸ The above conclusion was not easily deduced, for sodium fluoride, if ionised, should present no first order reflections from planes having three odd indices. Such planes did, in fact, give weak reflections. The way out of this difficulty involved theoretical considerations, including estimates of the disturbances due to temperature (subsequently applied to lithium fluoride), the objective value of which the present writer feels he is not competent to estimate. In view of the fundamental importance of the subject, most crystallographers would feel happier if the results of any future comparative investigation of the whole co-structural group of alkali haloids mutually confirmed each other, for there would then be a reasonable certainty that the theoretical considerations are congruent with the workings of nature.

Whilst it probes the structure more profoundly than a purely chemical method ever sets out to do, it does not at the present moment give any information on chemical properties or structure. For example, although the similarity of structure of carbon (diamond), silicon, and tin can be held to have chemical significance, and although we are possibly on the eve of absolutely trustworthy information concerning the existence or no of "ionisation" in crystals, there is, so far, no real information from X-ray sources on the mechanism of such chemical unions as are implied by the formula CH_4 , or the formula (SO_4) of the sulphate radicle, or by the commas characteristic of the formulæ $\text{MgSO}_4, 7\text{H}_2\text{O}$,



and $2\text{KF}, \text{SiF}_4$, or the significance of a happier variant of the latter, $\text{K}_2[\text{SiF}_6]$. It would appear that chemical information on all these points can only accrue by the X-ray method in so far as the unions are brought about by the transfer of one or more X-ray diffracting electrons.

During recent years there has been a tendency to jump to the conclusion that molecules disappear in a crystal and become parts of an indefinitely extended crystal molecule. X-Ray physicists have never claimed that their work decides the question one way or the other, although the close approach of the three oxygen atoms in the calcite structure could be interpreted, perhaps, as a sign that the (CO_3) group exists as an entity. At the present moment something more than mental inertia compels the view that molecules or ionic groups persist in a crystal; it will be time to revise the view when, say, it is the usual thing for a crystal of an ortho-compound to give a mixture of ortho- and para-derivatives on melting, or vice versa. A certain amount of pooling of affinity may exist in a crystal (and so lead to a very shadowy, indefinitely extended "molecule"), but to a degree that is at present quite vague and scarcely susceptible of discussion.

So far as crystallography is concerned, the result of the X-ray work is the proof that the abstract theory of crystal structure (built up by the efforts of Häuy, Frankenheim, Bravais, Sohncke, Fedorov, and Schönflies) faithfully embodies a concrete reality. The present interpretation is an atomic interpretation, because molecules are, so to speak, outside the terms of reference of the X-ray inquiry. Work on the infra-red²⁹ is susceptible of a molecular interpretation, but possibly other methods will have to be

²⁹ C. Schaefer and M. Schubert, *Ann. Physik*, 1916, [iv], **50**, 283, 339*, 1918, [iv], **55**, 397, 577; 1919, [iv], **59**, 583; *A.*, 1916, ii, 505; 1918, ii, 282, 315; K. Brieger, *ibid.*, 1918, [iv], **57**, 287; *A.*, ii, 37.

found before the molecular aspect of crystal structure becomes fully revealed.

The results already obtained are of such superlative importance as to make it desirable that the X-ray work shall continue along crystallographic lines and not altogether take other directions. There are signs, however, that future developments may not be so rapid. It would seem that the simpler cases are being exhausted and that great difficulties stand in the way of future progress. Many of the cases which have been examined defy any trustworthy interpretation.

Although further results can be expected from a more refined investigation of the simpler cases already elucidated, investigations on slightly less simple cases is the obvious next step. How are these cases to be selected? Past results have supplied an answer, but only on the negative side. Degree of complication evidently depends on two main factors, complexity of chemical composition and lack of crystal symmetry. The two factors are mysteriously interwoven, and may only be separated in a tentative manner for illustrative purposes. The orthorhombic sulphur and the hexagonal (?) graphite are less simple than any cubic element, but they are also less simple than the rhombohedral calcite. The tetragonal cassiterite (complicated enough) is simpler than the cubic garnet. The orthorhombic potassium sulphate, K_2SO_4 , is more complicated than the cubic spinel, Al_2MgO_4 . When the two factors are regarded singly, it appears likely that complexity increases in a kind of geometrical progression with the number of kinds of atoms and with degradation of symmetry. No successful interpretation has yet been offered for a substance containing four kinds of atoms (with the possible exception of Niggli's alum model) or for an orthorhombic, monoclinic, or anorthic crystal.

In the past, the proper choice of material for investigation was perhaps fairly obvious; elements and simple compounds crystallising in the cubic system invited inquiry. More recently, the selections have not been so fortunate. The selections have, perhaps, been guided by physical rather than chemical instincts. The present writer believes that a proper regard to both chemistry and physics is more likely to lead to happy selections, and that the real finger-post is symmetry.

Although many exceptions are known, it is, nevertheless, a statistical truth that everything strives towards symmetry in so far as the environment will allow. Chemical molecules take up symmetrical configurations—otherwise 99 per cent. would be theoretically resolvable into enantiomorphous configurations.

Again, the arrangement in a crystal tends towards symmetry. Most elements crystallise in the cubic, hexagonal, tetragonal, and rhombohedral systems. Binary molecules, like sodium chloride, possessing a rotational axis of symmetry, group themselves in highly symmetrical ways (the grouping possibly being facilitated by ionisation). Organic chemical molecules, which configurationally rarely possess more than a plane or centre of symmetry, generally arrange themselves during crystallisation according to a higher symmetry (45 per cent. in each of the orthorhombic and monoclinic systems). Unfortunately, this higher symmetry is frequently accompanied by grave complications, interpenetration of molecular or ionic space lattices giving rise to more general point systems, the elucidation of which becomes accordingly difficult. There is, however, a fairly well-represented class of substances in which the most probable stereochemical configuration has the same symmetry as the crystal form. Such structures are less likely to be complicated; the number of structural parameters should be relatively small. These are the substances which appear to be worthy of the immediate attention of X-ray workers. A few typical examples will serve as illustrations.

In the province of organic chemistry, molecules of carbon tetrabromide and tetraiodide, silicon tetraiodide, and hexamethylene-tetramine, $N_4(CH_2)_6$, have the symmetry of a regular tetrahedron, and the substances crystallise in the cubic system (carbon tetrabromide above 47°). The elucidation should be easier than that of garnet. In inorganic chemistry, there are many compounds, like potassium platinochloride and periodate, which are "tetragonal" configurationally and in crystallisation. In the rhombohedral system, in addition to calcite, there are numerous groups of compounds, of which the following formulæ illustrate examples: $Mg_2SiF_6 \cdot 6H_2O$, $MgPtI_6 \cdot 9H_2O$, $MgPtBr_6 \cdot 12H_2O$. In all these cases, the natural configurations for the separated parts, say, $[Mg_6H_{12}O]^{++}$ and $[SiF_6]^{--}$, are rhombohedral, and the structures will presumably involve two or four parameters more than in the case of calcite. However complicated the formulæ may appear, the structures can scarcely be as difficult as in a case like potassium sulphate, where a tetragonal molecule or SO_4 group is degraded to fit in with an orthorhombic type of symmetry.

With regard to the question whether the exploration of, say, carbon tetrabromide should reveal the quadrivalent nature of carbon, it seems certain that an appeal to a transfer of electrons will not help matters, for relative intensities can scarcely substantiate an assumption (transfer of electrons) concurrently with the value of the bromine parameter.

Tammann's Work on Diffusion and Reaction Limits: Chemical and Galvanic.

It may be stated at once that the work capitalises the interest that has always been attached to the property of diffusion in the solid state,³⁰ and has, no doubt, considerable metallurgical significance. Tammann³¹ shows that cast, untempered alloys, or, what amounts to the same thing, tempered alloys which have been subsequently subjected to harsh treatment (rolling, drawing into wire, hammering, and so forth), tend to behave incoherently towards chemical reagents, whilst tempered alloys take on themselves some of the properties of a compound. He presents a mass of experimental data which at least goes a long way towards proving that mixed crystals (not compounds in the formal sense) in certain simple, definite proportions resist chemical action in the same degree as is exhibited by the more dour constituent. This organised resistance is referred to an intimate atomic equilibrium, set up as a result of diffusion, whereby the structural space lattice loses the properties of a conglomerate and acquires that perfection of design which is characteristic of the structure of an uncontaminated metal or pure chemical compound. So much by way of introduction; we may now consider a few details, almost wholly restricted to gold alloys.

Chemical Behaviour of Well-tempered Alloys.—At both ordinary and at slightly elevated temperatures, well-tempered copper-gold and silver-gold alloys remain uncorroded in general and do not bring about any deposition of metal from solution when digested for a prolonged period with solutions of palladous chloride, platinous chloride, yellow ammonium sulphide, sodium disulphide, sulphur dissolved in carbon disulphide, sodium diselenide, picric acid, or alkaline solutions of sodium tartrate, provided the alloy contains 25 molecular per cent. or more of gold; if, however, the gold content sinks to 24 per cent., chemical reaction takes place. Again, with the silver-gold series of well-annealed mixed crystals, the limit of reaction for solutions of gold chloride, chromic, permanganic, and nitric acids lies sharp at the 50 molecular per cent. composition. Further, at the ordinary temperature, moist air containing hydrogen sulphide has no action on copper-gold alloys containing at least 25 molecular per cent. gold, but at temperatures higher than 100°, alloys of all compositions are gradually attacked,

³⁰ Compare "Diffusion in Solids," by C. H. Desch, *Brit. Assoc. Reports*, 1912, 348.

³¹ G. Tammann, *Zeitsch. anorg. Chem.*, 1919, **107**, 1-239; *Nachr. Ges. Wiss. Göttingen*, 1916-1919; *A.*, 1917-1919, ii.

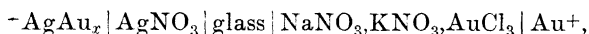
with the formation of oxide or sulphide of copper. This reactivity Tammann attributes to the enhanced rate of diffusion of copper and gold atoms, so that action is no longer restricted to the finest possible surface layer. Mercurous salts also attack the whole copper-gold series (pure gold excepted), even at the ordinary temperature; there is, however, a reaction limit in the matter of a precipitation of mercury from mercuric chloride at the composition 25 molecular per cent. gold. There is also a limit in the reaction of solutions of silver salts; in this case, it is not so sharply defined, lying between the limits 8—15 molecular per cent. gold. Presumably, by analogy, Tammann considers the upper limit as lying at $1/8$ gold (12.5 molecular per cent.).

With some reagents there is not merely an absolute resistance limit—there is also a relative resistance limit. Thus, boiling nitric acid removes the whole of the copper or silver from a gold alloy provided the gold content is less than $3/8$ mol.; if the composition lies between $3/8$ and $4/8$ gold, only part of the less noble metal can be extracted; if the composition lies between $4/8$ and $8/8$ gold, the specimen, as stated above for many other reagents, is wholly unattacked.

Chemical Behaviour of Untempered Alloys.—Several series of comparative experiments were made on the effect of tempering copper-gold alloys (having compositions close to the $4/8$ limit) on the sharpness of the limit of reaction. The reaction selected was the deposition of finely divided gold from a solution of aurous chloride. The reactants were sealed up in tubes and inspected from time to time, and the strips of alloy were subsequently tempered and digested afresh with solution. The results seem very convincing. Untempered strips ranging up to a 51 molecular per cent. gold content became stained in patches, owing to parts of the specimen having a less percentage composition than 50. If tempered at 900° for forty hours, an alloy containing 50.5 molecular per cent. of gold remains bright, whereas equally tempered alloys containing 49.5 per cent. or less become brown. It must, accordingly, be concluded that the reaction limit for the homogeneous mixed crystal lies at 50 molecular per cent.

The deleterious effect of cold-working a previously tempered "soft" alloy on the sharpness of the reaction limit is illustrated by a series of experiments on the action of sodium sulphide on silver-gold alloys. Well-tempered plates (0.5 mm. thick) exhibit a reaction limit within the narrow range 24.5—25.5 molecular per cent. gold. When the same plates had been rolled and beaten out to an order of thickness represented by 0.01 mm., discoloration took place even with a gold content of 55 molecular per cent.

Galvanic Potential.—The application of thermodynamic theory to a study of the dependence of polarisation potential on the composition of an alloy presupposes that the several kinds of metallic atoms can inter-diffuse with great rapidity. This condition is, however, not fulfilled at ordinary temperatures, so that mixed crystals may be expected to betray a definite resistance limit. This expectation was realised, for example, in the copper-gold and silver-gold series of alloys. The polarisation potential for "soft" tempered gold-silver alloys in an alloy|AgNO₃ solution|Ag element has the constant value 0.808 volt for all mixed crystals varying from 100 to 50 molecular per cent. gold, whilst the much lower value 0.71 volt is suddenly found for mixed crystals containing 49 per cent. gold. On the other hand, "hard" untempered alloys (non-homogeneous), whilst showing something of a break at the 50 per cent. composition, do not exhibit the constant value 0.808 volt for gold-rich series, but values fluctuating between 0.703 and 0.739. A series of investigations was made at higher temperatures. In the case of the element



it was found that the potential varies greatly with the temperature and changes with the time. The galvanometer readings first became independent of the time at 320°, and at this temperature the values showed no break at 50 per cent. composition, but varied continuously for the whole series of Au-Ag alloys. This fundamental difference of behaviour at low and high temperatures is in harmony with the differences already mentioned for "chemical" reactivities; they indicate that, at temperatures at which an active process of diffusion is out of the question, the chemical properties of metallic mixed crystals change discontinuously at certain definite concentrations. Tammann emphasises the point that these changes cannot be referred to the formation of chemical compounds in the formal sense, for the substances in question are miscible in all proportions and chemically similar. It may be added that the occlusion of hydrogen by mixed crystals of palladium and platinum reveals corresponding discontinuities.³²

Behaviour of Mixtures of Sodium Chloride and Silver Chloride.

—Although such mixed crystals cannot be obtained from aqueous solution, for obvious reasons, they are readily obtainable in any proportion from mixed fusions.³³ The process of leaching these mixed crystals has been studied by Tammann and Schmidt.³⁴ The

³² G. Tammann, *Nachr. Ges. Wiss. Göttingen*, 1918, 72; *A.*, ii, 293.

³³ C. Sandonnini, *Atti R. Accad. Lincei*, 1911, [v], 20, i, 758; *A.*, 1911, ii, 800.

³⁴ G. Tammann and K. W. Schmidt, *Nachr. Ges. Wiss. Göttingen*, 1918, 296; *A.*, ii, 396.

results depend greatly on whether the mixed crystals have or have not been tempered (that is, rendered homogeneous by holding at a temperature well below the melting point for a considerable time). Well-tempered crystals (powdered to a size less than 0.05 mm.) refuse to yield any sodium chloride provided the composition is at least $6/8\text{AgCl}$, whilst crystals ranging between $5/8\text{AgCl}$ and pure NaCl give up the whole of the sodium chloride. In the interval, $6/8$ — $5/8\text{AgCl}$ part of the sodium chloride is extractable.

Synopsis of Results.—The following table will indicate the comprehensive nature of Tammann's investigations and their general results. In every case the fraction refers to the second member of the metallic pair of components:

Components.	Chemical and galvanic reaction limits.		
Ag-Au	—	$2/8$	$4/8$
Cu-Au	$1/8$	$2/8$	$4/8$
Fe-V	—	—	$4/8$
Ag-Mn	—	$2/8$	—
Ag-Mg	$1/8$	—	—
*Zn-Ag	—	$2/8$	—
*Zn-Au	—	$2/8$	$4/8$
Pd-Au	—	—	$4/8$
Pd-Ag	—	—	$4/8$

* The alloys containing zinc appear to be complicated owing to the existence of "intermetallic compounds."

Tammann's Theoretical Interpretation.—The interpretation of the above interesting observations is naturally of a geometrical order. Only the sketchiest description can be given here. There are three space lattices in the cubic system: the cube (Tammann's "8-point lattice"), the centred cube ("9-point lattice"), and the face-centred cube ("14-point lattice"). For each of these lattices the most regular distribution ("well-tempered" distribution) can be worked out for two components, *A* and *B* (say, gold and copper, or gold and silver), or for three components, *A*, *B*, and *C* (say, sodium, silver, and chlorine), when present in the definite amounts implied by $1/8$, $2/8$, $3/8$, and $4/8$. Thus, in the case of a $2/8$ mixed crystal of gold and silver (for example, $\text{Au}:\text{Ag}=1:3$), the regular distribution for the face-centred lattice is that in which one of the four component cubic lattices is wholly occupied by gold atoms. It is apparently only in a well-tempered state that noble atoms will be in a position to protect less noble atoms, under which favourable conditions, for every noble atom present, the protection (which is not individually, but socially, organised) may extend beyond the limits 1:1 ($4/8$) and reach the limits 1:3 ($2/8$). The efficiency of the protection is worked out with a wealth of ingenuity;

it partly depends on the chemical nature of the dissolvent and partly on the nature of the space lattice. If properly protected, it is only the surface atoms which are within reach of the dissolvent. If, however, the temperature is sufficiently high, the boundary layer of noble atoms may lose their protective powers, on account of the high rate of inter-diffusion of space-lattice components, with the result that the structure is eventually deprived of its less noble elements.

General Conclusions.—In a comparison of the behaviour of alloys and mixed crystals of salts, Tammann points out that diffusion in the latter is extremely slow. Alloys can be thoroughly tempered at several hundred degrees below the melting point, but mixed crystals of compounds, as, for example, mixtures of sodium chloride and silver chloride, require more prolonged treatment at temperatures relatively nearer the melting point. The comparatively slow rate of diffusion of isomorphous compounds can also be demonstrated visually by selecting substances (say, azobenzene and dibenzyl) in which the rate of interpenetration can be measured by the advance of the coloured border. It is also pointed out that the anomalous double refraction of isomorphous mixtures of barium and lead or strontium nitrates is referable to the fact that deposition from aqueous solution occurs at temperatures so far below the melting points of the constituents that true equilibrium cannot be subsequently attained by a process of diffusion. Many kinds of observations are quoted showing that ordinary mixed crystals are scarcely ever homogeneous; this implies that the laws of dilute solutions are not rigorously applicable to "solid solutions."³⁵

³⁵ The above digest, somewhat inadequate for lack of space, was compiled from the only available original source, the paper printed in the *Zeitschrift für anorganische und allgemeine Chemie*. A comparison of that comprehensive review with the abstracts of his numerous papers in the *Göttingen Nachrichten* reveals the fact that a certain amount of revision has been undertaken by Tammann; thus, the previous statement that solutions of vanadic acid reveal an intermediate reaction limit for gold-copper mixtures at 3/8-gold appears to have been tacitly withdrawn. Again, earlier statements that "with the hexagonal Sb-Bi mixed crystals the rate of action of different reagents alters abruptly at multiples of 1/6" is likewise dropped; in the general interpretation suggested by Tammann, the stages, if any, should follow the rule of "eights," not of "sixths," since the lattice can scarcely be hexagonal, but is rather rhombohedral and pseudo-cubic. Moreover, it is difficult to see how an interpretation which holds for alloys typified by gold-silver, the constituents of which have the same space lattice, can be regarded as satisfactory in such a case as magnesium-silver in which the two-constituents exhibit fundamental differences of structure.

Some Crystallographic Researches.

The examination of the double selenates of the general formulæ $R_2Fe(SeO_4)_2 \cdot 6H_2O$ and $R_2Co(SeO_4)_2 \cdot 6H_2O$, in which R represents potassium, rubidium, cæsium, and ammonium, has been carried out by Tutton.³⁶ The investigation of the iron series was rendered very difficult owing to the instability of ferrous selenate. The work had to be carried out at as low a temperature as possible. The results confirm all the author's previous conclusions concerning the regular progressive effects of potassium, rubidium, and cæsium, and also the close similarity of the ammonium salts. On the other hand, doubts have been expressed by I. Langmuir³⁷ concerning the innate isomorphous replaceability of potassium and the ammonium radicle as being at variance with one of the deductions from his "octet theory" of electronic distribution.³⁸ The author attributes the isomorphism of potassium and ammonium sulphates to the mass-effect of the sulphate radicle, and he appeals to the difference in structure, as revealed by X-rays, of the cubic chlorides. It may be noted here that a similar appeal to the iodides neutralises the value of this evidence. Langmuir's paper, however, mainly deals with the more general aspects of isomorphism. Thus, he is led to expect isomorphism, as a result of similarity of electronic arrangement, between the following pairs of compounds, which, it will be observed, present the same general similarity of composition as Fedorov's "isotectonic" and Barker's "unusual" cases: NaF, MgO, MgF_2 , Na_2O , KCl, CaS, $CaCl_2$, K_2S , RbBr, SrSe, $SrBr_2$, Rb_2Se , CsI, BaTe, BaI_2 , Cs_2Te , N_2CO , $KCNO$, KN_3 , $NaHSO_4$, $CaHPO_4$, $KHSO_4$, $SrHPO_4$, $NaClO_3$, $CaSO_3$, $KHSO_3$, $SrHPO_3$, $Na_2S_2O_6$, $Ca_2P_2O_6$, $Na_2S_2O_7$, $Ca_2P_2O_7$, $MnSeO_4 \cdot 2H_2O$, $FeAsO_4 \cdot 2H_2O$. Relatively few of the above compounds appear to have been crystallographically examined, but Langmuir gives fairly convincing evidence in the cases already known. For example, Hull has at his suggestion definitely proved by means of X-rays that magnesia has the same cubic structure as sodium fluoride and rock salt.

A brief paper by Bowen³⁹ serves to clear up the apparently irregular optical behaviour of the mineral torbernite,



which under crossed Nicols only yields red and purple interference

³⁶ A. E. H. Tutton, *Phil. Trans.*, 1919, [A], **218**, 395; *A.*, ii, 346; *Proc. Roy. Soc.*, 1919, [A], **96**, 156; *A.*, ii, 417.

³⁷ *J. Amer. Chem. Soc.*, 1919, **41**, 1543; *A.*, ii, 506.

³⁸ *Idem*, *ibid.*, 868; *A.*, ii, 328.

³⁹ N. L. Bowen, *Amer. J. Sci.*, 1919, [iv], **48**, 195.

tints, even when the sections are so thin that grey of the first order would be expected. It is found that the mineral is negative for short wave-lengths and positive for longer wave-lengths, the wave-length for isotropism being 0.515μ .

An elegant study of the natural and artificial etching figures on crystals of the calcite group of minerals⁴⁰ admirably illustrates the law of symmetry; in all cases, the symmetry of form and disposition of the figure is in accordance with true rhombohedral symmetry. Comparative experiments on cleavage plates betray degrees of resemblance represented by calcite, magnesite, rhodochrosite, chalybite; . . . calamine. Apparently not cognisant of the work of Goldschmidt and Wright, the author records some observations which illustrate the law of polarity.⁴¹

The rotatory power of sodium chlorate crystals, both when pure and when coloured with "extra China-blue," has been determined by Perucca,⁴² who observed in different azimuths variations in the rotatory value of the coloured crystals which amounted to some 25 per cent. Variations were also observed for the pure crystals; the mean value for $[\alpha]_D^{18}$ is $+3.07^\circ$.

A crystal of sulphur from a unique source (a mixture of a hot alcoholic solution of ammonium polysulphide, benzonitrile, hydroxylamine hydrochloride, and ether) has been identified, and measured by F. R. von Bichowsky,⁴³ who also contributes a valuable statistical summary of the various forms which have been observed. The author remarks on the prevalence of odd numbers in the indices at the expense of even numbers, the interpretation of which has been given by G. Friedel⁴⁴ as a striking example of the Bravais principle.

A paper by G. F. H. Smith and R. H. Solly⁴⁵ on the perplexing form development of sartorite raises fundamental questions of crystal structure. The authors conclude that the crystals betray the interpenetration of three distinct space lattices, one of which is monoclinic, the other two anorthic. No doubt the authors have examined the question whether the simpler interpretation, offered by Fedorov⁴⁶ for the somewhat similar case of calaverite, is relevant or no; but, in any case, it seems to the Reporter that one of the crystals (preferably No. 1) should be crushed up and submitted to X-radiation by the Debye-Scherrer-Hull method—the angular

⁴⁰ A. P. Honess, *Amer. J. Sci.*, 1918, [iv], **45**, 201.

⁴¹ *Ann. Report*, 1917, 247.

⁴² E. Perucca, *Nuovo Cim.*, 1919, [vi], **18**, ii, 112; *A.*, ii, 487.

⁴³ *J. Washington Acad. Sci.*, 1919, **9**, 126; *A.*, ii, 189.

⁴⁴ *Bull. Soc. franç. Min.*, 1907, **30**, 365.

⁴⁵ *Min. Mag.*, 1919, **18**, 259.

⁴⁶ *Zeitsch. Kryst. Min.*, 1903, **37**, 611.

differences in the space lattices, inferred by the authors, might allow of a definite substantiation of the correctness of their interpretation.

The announcement, some nine months ago, of the death of Professor E. S. Fedorov, of Petrograd, came as a heavy blow to his many admirers. A brief appreciation is postponed from this Report in the hope that he may still be with us, actively furthering the progress of science by his rare genius.

T. V. BARKER.

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